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Investigation into Levels of Dioxins, Furans, Polychlorinated Biphenyls and Brominated Flame Retardants in Fishery Products in Ireland

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ABBREVIATIONS AND GLOSSARY

Ah receptor	Aryl hydrocarbon (Ah) receptor
b.w.	Body weight
BB	Body burden
BDE	Brominated diphenylether (Polybrominated diphenylether, PBDE)
BFRs	Brominated flame retardants
BTBPE	Bis(2,4,6-tribromophenoxy)ethane
Congener	Term referring to one of many configurations of a common chemical structure
DBDPE	Decabromodiphenylethane
DL-PCB	Dioxin-like PCB
EC	European Community
EFSA	European Food Safety Authority
FSAI	Food Safety Authority of Ireland
HBB	Hexabromobenzene
HBCD	Hexabromocyclododecane
HpCB	Heptachlorobiphenyl
HpCDD	Heptachlorodibenzo-*p*-dioxin
HpCDF	Heptachlorodibenzofuran
HSE	Health Service Executive (formerly the Health Boards)
HxCB	Hexachlorobiphenyl
HxCDD	Hexachlorodibenzo-*p*-dioxin
HxCDF	Hexachlorodibenzofuran
ICES-6	International Council for the Exploration of the Seas-6 Indicator PCBs
ICES-7	International Council for the Exploration of the Seas-7 Indicator PCBs
JECFA	FAO/WHO Joint Expert Committee Food Additives and Contaminants
LOD	Limit of Detection
LOQ	Limit of Quantification/Quantitation
Lower-bound	Analytical results below the LOD set at zero for calculation purposes
MI	Marine Institute
NATO	North Atlantic Treaty Organisation
NATO-CCMS	NATO Committee on the Challenges of Modern Society
NDL-PCB	Non-dioxin-like PCB
ng	Nanogram (0.000000001 g, 10^{-9} g or one billionth of a gram)
ng/g	Nanogram per gram
ng/kg	Nanogram per kilogram
Non-oily fish	A fish species in which fat is predominantly located in the liver. The fat content of other tissues is below 2%
OCDD	Octachlorodibenzo-*p*-dioxin
OCDF	Octachlorodibenzofuran
Oily fish	A fish species with fat distributed throughout the tissues, as opposed to in the liver only. The fat content ranges between 2 and 30%
PBB	Polybrominated biphenyls

PBDDs	Polybrominated dibenzo-*p*-dioxins
PBDEs	Polybrominated diphenylethers
PBDFs	Polybrominated dibenzofurans
PCBs	Polychlorinated biphenyls
PCDD/F	Abbreviation for PCDDs and PCDFs
PCDDs	Polychlorinated dibenzo-*p*-dioxins
PCDFs	Polychlorinated dibenzofurans
pg	Picogram (0.000000000001 g, 10^{-12} g or one trillionth of a gram)
pg/g	Picogram per gram
pg/kg	Picogram per kilogram
PnCB	Pentachlorobiphenyl
PnCDD	Pentachlorodibenzo-*p*-dioxin
PnCDF	Pentachlorodibenzofuran
POP	Persistent Organic Pollutant
ppb	Parts per billion (equal to ng/g or µg/kg)
PTMI	Provisional Tolerable Monthly Intake
PUFA	Poly unsaturated fatty acids
PXB	Mixed halogenated biphenyls
PXDD/F	Mixed halogenated dioxins and furans
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals Regulation
RoHS	Restriction of Hazardous Substances Directive
SCF	Scientific Committee on Food
SCOOP	Scientific Cooperation Task of the EC
SD	Standard deviation
TBBP-A	Tetrabromo-bisphenol A
TCB	Tetrachlorobiphenyl
TCDD	Tetrachlorodibenzo-*p*-dioxin
TCDF	Tetrachlorodibenzofuran
TDI	Tolerable Daily Intake
TEF	Toxic equivalency factor
TEQ	Toxicity equivalent
TWI	Tolerable Weekly Intake
Upper-bound	Analytical results below the LOQ set at the LOQ value for calculation purposes
w.w.	Wet weight or whole weight
WHO	World Health Organization
WHO-ECEH	European Centre for Environment and Health of the World Health Organization
µg	Microgram (0.000001 g)
Σ	Sum
Σ6PCB	Sum of 6 indicator PCBs (28, 52, 101,138, 153 and 180)
Σ7PCB	Sum of 7 indicator PCBs (28, 52, 101, 118, 138, 153 and 180)

1. SUMMARY

The Food Safety Authority of Ireland in collaboration with the Marine Institute (MI) has carried out a further surveillance study of levels of dioxins (PCDDs), furans (PCDFs) and polychlorinated biphenyls (PCBs) in fish, in addition to those already carried out in 2001 and 2004. The study was carried out in a variety of wild and farmed finfish species and also prawns and cultivated mussels available on the Irish market. It was undertaken because of concern about the possible effects on human health of these biopersistent environmental contaminants, known to be present in a number of foodstuffs including, in particular, fish, meat, eggs and dairy products. Furthermore, the study also proactively monitored fish and other seafood for a number of emerging new contaminants, in order to contribute to the knowledge base on the occurrence of these contaminants in food and to aid national and international efforts in their management. These include the brominated flame retardants and related compounds, some of which are known to be persistent and hence, like PCDDs, PCDFs and PCBs, are regarded as persistent organic pollutants (POPs).

The study showed that levels of PCDDs, PCDFs and PCBs (both DL-PCBs and indicator PCBs) in Irish fish and other seafood are well below the limits laid down for these POPs in Council Regulation 1881/2006, as amended. The mean sum of PCDD/F and DL-PCBs in farmed salmon (the species with the highest content of these contaminants) was 1.47 $\pm$ 0.55 ng WHO TEQ/kg wet weight, compared with a legal limit of 6.5 ng/kg wet weight. Legal limits for the sum of the six indicator PCBs (PCB-28, 52, 101, 138, 153, and 180) have been recently introduced into legislation. The levels of these indicator pollutants were also well below the statutory limits, with 11.1 $\pm$ 4.06 µg/kg wet weight being detected in farmed salmon, compared with the legal limit of 75 µg/kg wet weight. Levels of PCDDs, PCDFs and PCBs in the non-oily marine species surveyed, and also in mussels and crustaceans, were much lower than those found in the four oily fish species surveyed (salmon, sea reared trout, mackerel and tuna). This is not unexpected since these lipophilic contaminants accumulate in fatty tissues and therefore will be higher in foods with a relatively high fat content.

The results of this study are in line with those from the previous FSAI studies on dioxin levels in fish and also studies on meat, milk and eggs, and confirm that dioxin levels in these foods are relatively low compared with data for similar products from more industrialised countries in the European Union. Comparison of the levels of PCDDs, PCDFs and PCBs in farmed salmon from this study showed a marked decline relative to the levels found in studies carried out in 2001 and 2004. This could be attributed to more stringent controls on industrial emissions of these POPs, together with the maximum limits introduced for feed used in aquaculture, feed being an important source of contamination in farmed salmon prior to introductions of such limits. Data were not available for mackerel and tuna in 2001. Comparison of the data from 2004 and 2010 also showed lower concentrations of PCDDs and PCDFs in albacore tuna than in 2004. However, inferences about temporal trends of environmental concentrations of these substances should not be drawn from such a surveillance sampling programme as many other factors also influence contaminant burdens. Overall, the FSAI concludes that current exposure of Irish consumers to dioxins and PCBs is likely to be well below the Tolerable Weekly Intake for the sum of PCDDs, PCDFs and DL-PCBs of 14 pg WHO-TEQ/kg body weight established by the EC Scientific Committee on Food or the Provisional Monthly Tolerable Intake of 70 pg WHO-TEQ/kg established by the World Health Organization (WHO).

Of the brominated flame retardants covered in this survey, the polybrominated diphenyl ethers (BDEs) and hexabromocyclododecane (HBCD) were detected in most fish samples. The highest concentrations of total BDE (sum of the 26 congeners analysed in the study) were observed in

farmed Atlantic salmon (1.81 µg/kg wet weight), followed by mackerel and sea reared trout (1.02 µg/kg wet weight in both species) and fresh tuna (0.46 µg/kg wet weight). Non-oily white fish, mussels and prawns had lower levels, although there was some variation between the species. The result for the single pooled sample of prawns was notable for the fact that the only BDE detected in this species was BDE 209, at a level of 0.1 µg/kg wet weight, which was the highest concentration of this congener detected in any sample in the study. In the other species surveyed, the predominant BDEs were BDEs 47, 49, 99, 100, 154 and 155. There was an indication of a general decline in levels of BDEs over the period 2004 - 2010, which coincides with the regulatory controls introduced for these compounds over the last decade, including the banning of a number of the more bioaccummulative congeners such as those primarily present in pentaBDE mixtures.

α-HBCD was the predominant hexabromocyclododecane isomer detected, the β- and γ-isomers were generally below the LOQ or were only found in trace amounts. α-HBCD was detected above the LOQ in all samples of mackerel, farmed salmon, sea reared trout, tuna and farmed mussels analysed. Levels of total HBCD (sum of α-, β- and γ-HBCD) in farmed salmon of 0.55 ± 0.2 µg/kg fresh weight were lower than those found in the 2004 FSAI survey, which reported levels of 1.17 ± 0.26 µg/kg fresh weight.

Polybrominated biphenyls (PBBs) were detected at low levels in a number of samples of oily fish and also in farmed mussels, but not in non-oily fish, with the exception of plaice. Tetrabromobisphenol A (TBBP-A) and hexabromobenzene (HBB) were not detected in any sample at levels above the LOQ, while bis(2,4,6-tribromophenoxy)ethane (BTBPE) was detected at the LOQ (0.01 µg/kg) in one sample of mussels and in a sea reared trout sample. Decabromodiphenylethane (DBDPE) was detected in two monkfish samples and a whiting sample, again at levels around the LOQ.

Of the brominated dioxins (PBDDs/PBDFs), the most commonly detected brominated congener was 1,2,3,4,6,7,8-HeptabromoBDF, detected in one or more samples from every species investigated in this study. For the majority of species, this was the only brominated congener detected. However, farmed mussels, and to a lesser extent, farmed salmon and sea reared trout contained measurable levels of the other brominated dioxin congeners. The PBDFs predominated, with mussels containing 2,3,7-TriBDD, 2,3,8-TriBDF, 2,3,7,8-TetraBDF,1,2,3,7,8-PentaBDF and 2,3,4,7,8-PentaBDF as well as 1,2,3,4,6,7,8-HeptabromoBDF. Similar findings were reported by the FSAI in 2010 in other food of animal origin. The mean derived upperbound WHO TEQ attributable to PBBDs and PBBFs for mussels was 0.020 ± 0.003, for salmon 0.020 ± 0.002 and for sea reared trout 0.022 ± 0.006. Of the mixed halogenated dioxins and furans measured, only 2-B-7, 8-CDD and 2-B-7, 8-CDF were found in any sample above the LOQ, and essentially only in farmed mussels. Four of the six mixed halogenated biphenyls (PXBs) measured in the study, PXB 105, PXB 118, PXB 126 and PXB 156, were found in mackerel, salmon, sea reared trout and tuna and occasionally in trace amounts in one or more samples of the other species investigated in the study, PXB 118 being the congener found at the highest level.

The FSAI concludes, taking into consideration recent hazard or risk assessments carried out by the European Food Safety Authority (EFSA) on a number of brominated POPs, that it is unlikely that intake of any of these brominated flame retardants, brominated or mixed halogenated dioxins, furans or biphenyls from fish is of health concern for the Irish population. However, with the banning/ introduction of restrictions on the use of all BDE commercial flame retardant mixtures and certain other brominated flame retardants, e.g. HBCD, in the European Union, the use and production of alternative substances is predicted to increase, and future surveillance programs should closely monitor any trends in Irish produce.

The levels of POP contaminants were somewhat higher in the oily fish examined in this survey, namely farmed salmon, sea reared trout, mackerel and tuna, compared with the extensive range of non-oily fish such as cod, hake, lemon sole and whiting also investigated. There is however, evidence that fish consumption, especially of oily fish, benefits the cardiovascular system, and also brain and eye development in the fetus and infant, due to the high content of omega-3 polyunsaturated fatty acids (PUFAs). The FSAI therefore recommends that consumers should eat at least two portions of fish per week including at least one serving of oily fish, e.g. salmon, trout, herring or mackerel.

The full study report follows, providing further sampling details, analytical methodologies and discussion of the resulting datasets.

2. BACKGROUND

The FSAI has a statutory responsibility to ensure the safety of food consumed, distributed, produced and sold on the Irish market. In this respect, the FSAI co-ordinates the collation of food safety surveillance information from laboratories run by its official agents, the Health Service Executive (HSE), the Department of Agriculture, Food and the Marine, the Marine Institute, the National Standards Authority of Ireland, the Sea-Fisheries Protection Authority, the County Councils and City Councils. The FSAI also conducts targeted food safety surveillance in areas where potential safety issues have been identified and/or on food contaminants such as dioxins.

This report provides the results of a targeted surveillance study undertaken in 2010 - 2011 in collaboration with the Marine Institute on levels of chlorinated dioxins (PCDDs) and furans (PCDFs), brominated dioxins (PBDDs) and furans (PBDFs), polychlorinated biphenyls (PCBs), polybrominated biphenyls (PBBs), mixed halogenated dioxins and furans (PXDD/Fs), mixed halogenated biphenyls (PXBs), polybrominated diphenyl esters (PBDEs), hexabromocyclododecane enantiomers (HBCD enantiomers), decabromodiphenylethane, hexabromobenzene, bis(2,4,6-tribromophenoxy)ethane and tetrabromo-bisphenol A (TBBP-A) in a variety of fishery products available on the Irish market. A number of these chemical contaminants are known to be persistent in the environment and in the food chain and hence are described as persistent organic pollutants (POPs). Moreover, long range atmospheric transport leads to many POPs being widely distributed around the globe. In recent years, there has been public debate concerning the health risks to consumers associated with POPs such as dioxins in certain species of fish, although potential risks are counterbalanced by the well-known nutritional benefits of eating fish, in particular oily fish[1]. Consumption of oily fish benefits the cardiovascular system, and also brain and eye development in the fetus and infant, due to the high content of omega-3 polyunsaturated fatty acids. The FSAI recommends that consumers should eat at least two portions of fish per week, including at least one serving of oily fish, e.g. salmon, trout, herring or mackerel.

The present work builds on previous studies carried out by the FSAI into levels of PCDD/Fs, PCBs and BDEs in milk, fish/fish oils, meat and eggs [2, 3, 4, 5, 6, 7], and was undertaken against the background of increased awareness in the European Union of the possible health risks posed by these substances in the food chain. It also reflects Ireland's participation in the ongoing EC monitoring programme for the background presence of dioxins, furans and dioxin-like PCBs in foodstuffs. In 2010, EFSA received a mandate from the European Commission to collect and analyse, on a continuous basis, all available data on dioxins and PCBs in food and feed, and data from the above studies have been reported to EFSA as part of this programme. The present study further includes compounds recommended by EFSA in 2006[8] for inclusion in the core group of brominated flame retardants (BFRs) of a European monitoring programme for feed and food, due to the production volumes, the occurrence of the chemical compounds in food and feed, their persistence in the environment and their toxicity.

Monitoring of residues and environmental contaminants such as trace metals, indicator PCBs and certain organochlorine pesticides in fish and shellfish is also undertaken by the Marine Institute as part of a service contract with the FSAI and is reported on an ongoing basis[9].

2.1 Dioxins and Furans

The term 'dioxins' covers a group of 75 polychlorinated dibenzo-p-dioxin (PCDD) and 135 polychlorinated dibenzofuran (PCDF) congeners, 17 of which are of toxicological concern. Exposure to dioxins can result in a wide range of toxic responses, including dermal toxicity (chloracne), immunotoxicity, carcinogenicity, reproductive toxicity and possible neurobehavioral (cognitive) effects, as reported by the EU Scientific Committee on Food (SCF), the predecessor of EFSA[10,11]. Studies on children exposed *in utero* to dioxins are reported to have shown persistent endocrine and developmental changes (SCF, 2000). The toxicological effects of dioxins are thought to arise due to binding to a specific receptor protein within cells, the aryl hydrocarbon (Ah) receptor, present in most tissues of animals and humans. The most toxic dioxin congener is 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin (TCDD) and is classified by the International Agency for Research on Cancer (IARC) and other international organisations as a known human carcinogen. By analogy, other dioxins are therefore considered as presumed carcinogens. The SCF, in line with the WHO, has concluded however, that the carcinogenic effect of dioxins does not occur at levels below a certain threshold[10,11].

Dioxins are chlorinated environmental contaminants and have no known commercial applications, other than in the preparation of analytical standards and research materials. They are formed during combustion processes, for example, in the incineration of municipal waste, although natural combustion processes such as forest fires and bonfires may also result in dioxin formation. They can also occur as by-products of industrial processes, for example production and use of pentachlorophenol-containing wood preservatives, production and use of certain herbicides and bleaching of paper pulp using chlorine. Dioxins have been identified in almost all environmental compartments as a result of these emissions. Emissions of dioxins to air may ultimately result in deposition in the terrestrial environment and in aquatic sediments, followed by uptake into the food chain, e.g. by ruminants and fish.

Dioxins are highly resistant to degradation processes in the environment and consequently persist in the environmental compartments where they have been deposited. This in part is due to their lipophilic characteristics, which can result in accumulation in the fatty tissues of the primary intake species e.g. cattle or fish. Approximately 90% of human exposure to dioxins and furans results from the consumption of contaminated food[10,12]. Exposure by other routes, such as inhalation and ingestion of particles from air, ingestion of contaminated soil and dermal absorption normally contributes less than 10% of daily intake[10].

Humans are considered the ultimate consumers in the food chain, and accumulate dioxins in body tissues primarily as a result of exposure via food. In the case of cows or other lactating species, high levels of dioxins can potentially occur in milk (specifically in milk fat) and consequentially also in cream and in milk products such as cheese, in addition to accumulation within carcass meat. In fish, levels are usually higher in fatty tissues such as the liver and consequently, levels can be more elevated in fish liver oils. In an assessment of dietary intake of dioxins and related PCBs by the population of EU Member States, carried out in 2000 as a Scientific Cooperation (SCOOP) task, it was reported that the fraction of the dietary intake of dioxins contributed by these foods was: fish and fish products (2 – 63%), meat and meat products (6-32%); milk and dairy products (16-39%), with fruit and vegetables providing only a minor contribution to human intake[13]. More recently, EFSA has reported that for most adult population groups for which data were available (34 out of 40 groups), fish and seafood products was the food group contributing most to total exposure (30.2-75.0 %), followed either by meat and meat products (8.8-34.4 %) or milk and dairy products (7.3-24.6 %)[14]. In the remaining six population groups, meat and meat products were the

highest contributing group to exposure (35.4-37.7 %). In most infant and toddler populations, milk and dairy products (27.5-49.6 %) made the most significant contribution (35.4-37.7 %), followed by foods for infants and young children (21.7-30.9 %) and in toddlers by either fish and seafood products (10.7-35.8 %) or by meat and meat products (10.4-33.7 %)[14].

2.2 PCBs

Polychlorinated biphenyls or PCBs are a group of extremely stable aromatic chlorinated compounds which, like dioxins, are relatively resistant to biological degradation and hence persist and accumulate in the environment and in the food chain. There are 209 structurally possible PCB compounds (congeners), with one to ten chlorine atoms per molecule. They have excellent electrical and heat transfer properties, which led to their widespread use in a variety of industrial, commercial and domestic applications. The production and use of PCBs has been discontinued in most countries, due to concern about their toxicity and persistence, but large amounts remain in electrical equipment, plastic products, buildings and the environment. Incorrect disposal of such material can result in continued release to the environment, adding to existing levels present as a consequence of past releases.

As a class, PCBs are generally regarded as having potentially adverse effects on health, with particular concern being expressed about the 12 so-called dioxin-like PCBs (DL-PCBs). This group of non-ortho (PCBs 77, 81, 126, 169) and mono-ortho (PCBs 105, 114, 118, 123, 156, 157, 167, 189) PCBs are assumed to have essentially the same toxicity potential as dioxins and furans, since they also bind to the Ah receptor. Other PCBs (non-dioxin-like PCBs) (NDL-PCBs) do not exert their toxicological effects via binding to the Ah receptor but nonetheless are associated with a wide spectrum of toxic responses. They have been evaluated by a number of regulatory bodies including EFSA, who noted that environmental PCB exposure may result in adverse reproductive outcomes, delayed neurodevelopment and impairment of the immune system, as well as a possible increased risk of cancer[15].

The so-called marker or indicator PCBs have been used as indicators of the total PCB content or body burden of environmental biota, food and human tissue. The most frequent approach is to use either the total level of six or seven of the most commonly occurring PCBs (ICES-7 (International Council for the Exploration of the Seas) indicator PCBs, PCBs 28, 52, 101, 118, 138, 153 and 180, or PCBs 28, 52, 101, 138, 153 and 180 if the DL-PCB 118 from the ICES-7 group is excluded). Maximum levels for the six indicator PCBs have recently been introduced into legislation, see Section 2.5 of this report and Table 3. As noted by EFSA, these particular PCBs, with the exception of PCB-118, were not selected because of their particular toxicity but because they can act as markers of the technical PCB mixtures used in the past which are the main sources of PCB exposure[15]. The PCB pattern found in environmental and human samples is however, affected by biodegradation and photodegradation as well as bioaccumulation and metabolism, and hence, is different from that of commercial PCB mixtures on which the majority of toxicological studies have been carried out[15].

2.3 Toxic Equivalence Factors for Dioxins and Dioxin-like PCBs

The toxicity of individual PCDDs, PCDFs and the dioxin-like PCB congeners are expressed using toxic equivalence factors (TEFs) (see Tables 1 and 2) representing the relative toxicity of the compound being measured to the most toxic dioxin congener, TCDD. This in turn reflects the relative strength of binding to the Ah receptor. It should be noted however that the toxicity of many of these substances, both dioxins and PCBs, has not been extensively evaluated.

An arbitrary TEF of 1 is assigned to TCDD, and by multiplying the analytically determined concentrations of each congener in a sample, by its corresponding TEF, individual toxicity equivalents (TEQs) are determined. Summing the contribution from each congener, the total TEQ value of the sample can be obtained using the following equation:

TEQ = (PCDDi × TEFi) + (PCDFi × TEFi) + (*dioxin-like* PCBi × TEFi)

Several different TEF schemes have been proposed. For many years, the most widely used schemes were that of NATO/CCMS (NATO/CCMS, 1988), giving the so-called International TEFs (I-TEFs) for PCDDs and PCDFs and the WHO-ECEH (European Centre for Environment and Health of the WHO) scheme for PCBs[16]. In 1998, WHO-ECEH proposed an alternative scheme of WHO-TEFs for PCDDs, PCDFs and DL-PCBs, which to date, has been the most commonly used scheme[17]. Dioxin TEQ values for food and human samples based on WHO-TEFs are approximately 10-20% higher than those obtained by using the I-TEFs of NATO/CCMS. In 2005, the WHO re-evaluated the WHO-TEFs proposed in 1998 and adjusted the TEFs for a number of compounds[18]. European legislative limits for dioxins and DL-PCBs are now based on the 2005 WHO-TEFs (Tables 1 and 2) and the results provided in this report reflect the 2005 scheme, except where otherwise stated.

Table 1: Toxic Equivalence Factors (TEFs) for dioxins

PCDDs and PCDFs	Toxic Equivalency Factor (TEF)		
	I-TEF	WHO-TEF1998	WHO-TEF 2005
2,3,7,8-TCDD	1	1	1
1,2,3,7,8-PnCDD	0.5	1	1
1,2,3,4,7,8-HxCDD	0.1	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01	0.01
OCDD	0.001	0.0001	0.0003
2,3,7,8-TCDF	0.1	0.1	0.1
1,2,3,7,8-PnCDF	0.05	0.05	0.03
2,3,4,7,8-PnCDF	0.5	0.5	0.3
1,2,3,4,7,8-HxCDF	0.1	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01	0.01
OCDF	0.001	0.0001	0.0003

Abbreviations: PnCDD, pentachlorodibenzo-p-dioxin; HxCDD, hexachlorodibenzo-p-dioxin; HpCDD, heptachlorodibenzo-p-dioxin; OCDD, octachlorodibenzo-p-dioxin; PnCDF, pentachlorodibenzofuran; HxCDF, hexachlorodibenzofuran; HpCDF, heptachlorodibenzofuran; OCDF, octachlorodibenzofuran

Table 2: Toxic Equivalence Factors (TEFs) for dioxin-like PCBs (IUPAC No. in parenthesis)

PCBs	Toxic Equivalency Factor (TEF)		
	I-TEF	WHO-TEF 1998	WHO-TEF 2005
Non-*ortho* PCBs			
3,3',4,4'-TCB (77)	0.0005	0.0001	0.0001
3,4,4',5-TCB (81)	-	0.0001	0.0003
3,3',4,4',5-PnCB (126)	0.1	0.1	0.1
3,3',4,4',5,5'-HxCB (169)	0.01	0.01	0.03
Mono-*ortho* PCBs			
2,3,3',4,4'-PnCB (105)	0.0001	0.0001	0.00003
2,3,4,4',5-PnCB (114)	0.0005	0.0005	0.00003
2,3',4,4',5-PnCB (118)	0.0001	0.0001	0.00003
2,3,4,4'5-PnCB (123)	0.0001	0.0001	0.00003
2,3,3',4,4',5-HxCB (156)	0.0005	0.0005	0.00003
2,3,3',4,4',5'-HxCB (157)	0.0005	0.0005	0.00003
2,3',4,4',5,5'-HxCB (167)	0.00001	0.00001	0.00003
2,3,3',4,4',5,5'-HpCB (189)	0.0001	0.0001	0.00003
D-*ortho* PCBs			
2,2',3,3',4,4',5-HpCB (170)	0.0001	0.0001	-
2,2',3,4,4',5,5'-HpCB (180)	0.00001	0.00001	-
Abbreviations: TCB, tetrachlorobiphenyl; PnCB, pentachlorobiphenyl; HxCB, hexachlorobiphenyl; HpCB, heptachlorobiphenyl			

2.4 Assessment of the Risks to Health due to Dioxins, Furans and PCBs in Food

The SCF has carried out a risk assessment of dioxins, furans and DL-PCBs in food[10,11] and as a consequence, they concluded that the Tolerable Weekly Intake (TWI) for PCDDs, PCDFs and DL-PCBs should be no more than 14 pg WHO-TEQ/kg body weight (b.w.). This is very similar to the Provisional Tolerable Monthly Intake (PTMI) of 70 pg/kg b.w. per month derived by the FAO/WHO Joint Expert Committee on Food Additives and Contaminants (JECFA)[19]. It has been stated that the European average dietary intake is 1.2 to 3.0 pg WHO-TEQ/kg b.w./day, which translates into a weekly intake of between 8.4 and 21 pg WHO-TEQ/kg b.w. The upper end of this range exceeds the TWI as established by the SCF.

However, several studies carried out by the FSAI have indicated that levels of dioxins, furans and PCBs in Irish food are relatively low. In a recent report[7] on levels of a number of persistent organic pollutants including PCDDs, PCDFs and PCBs in milk, carcass (animal) fat, eggs and liver produced in Ireland, levels of PCDDs, PCDFs and DL-PCBs in farm milk ranged from 0.37 – 0.66 pg/g fat, expressed as total WHO-TEFs (1998). Levels in carcass fat from several species ranged from 0.12 – 0.88 pg/g fat, while levels in eggs ranged from 0.20 – 0.72 pg/g fat and in avian, porcine and bovine liver from 0.25 –1.72 pg/g fat. All of these levels were well below the existing legislative limits for these foods, as shown in Table 3[1]. Higher levels were found in ovine liver, at 4.25 – 16.39 pg/g fat. Similarly, in a 2007 FSAI study of a number of POPs in fish and fishery products available on the Irish market, levels of PCDDs, PCDFs and DL-PCBs expressed as total WHO-TEQs ranged from 0.05 – 2.15 pg/g WHO TEQ, which can be compared with the legislative limit of 8 pg/g wet weight (8 ng WHO TEQ/kg wet weight) for the sum of PCDDs, PCDFs and DL-PCBs (1998 WHO-TEQ, equivalent to 6.5 pg/g wet weight 2005 WHO-TEQ).

These studies indicate that levels of dioxins, furans and DL-PCBs found in Irish milk, fish and meat are lower than those found in comparable foodstuffs from the more industrialised EC countries. Hence, it is likely that the exposure of the Irish population to dioxins in food is less than the European average. Intake estimates made in the study on milk, carcass (animal) fat, eggs and liver for dioxins, furans and NDL-PCBs reported above indicate that exposure of the Irish adult population to these pollutants, at 17% and 70% of the TWI for average and above average Irish consumers, respectively, are below the European average, although this estimate is based solely on consumption of Irish produce and does not take into account intake from imported foodstuffs or other non-food sources[7].

A risk assessment for the non-dioxin-like-PCBs (NDL-PCBs) in food has also been carried out recently by the Scientific Panel on Contaminants of EFSA, to include identification of the most relevant/sensitive toxicological endpoints for the PCB-congener patterns usually found in food[20]. EFSA concluded that simultaneous exposure to NDL-PCBs and dioxin-like compounds makes the interpretation of the results of the toxicological and epidemiological studies very difficult, in relation to the toxicity of the non-dioxin-like PCBs. Overall, the Panel concluded that further research and additional data are needed to better evaluate adverse effects from NDL-PCBs, and a continuing effort to lower the levels of these contaminants in food is warranted.

[1] To note that values given in Table 3 are in 2005 WHO-TEQs

2.5 Legislation on Dioxins, Furans and PCBs in Food

Given that the weekly average dietary intake of dioxins by at least some of the European population is thought to exceed the TWI established by the SCF, on a European scale, it is desirable to reduce the exposure of the population to dioxins. In 2001, the European Commission (E.C.) published its Community strategy for dioxins, furans and polychlorinated biphenyls, aimed at achieving a reduction in human exposure to dioxins and PCBs (European Commission, 2001)[21]. As part of this reduction strategy, the EC has introduced maximum levels for PCDDs, PCDFs and DL-PCBs in foodstuffs, via Council Regulation (EC) No. 1881/2006[22], setting maximum levels for certain contaminants in foodstuffs, as amended by Regulation 565/2008/EC[23]. Maximum levels for the six indicator PCBs, PCB28, PCB52, PCB101, PCB138, PCB153 and PCB180, have also been introduced into Regulation 1881/2006, via amending Regulation 1259/2011[24]. Table 3 shows the maximum levels established in this Regulation for dioxins (sum of PCDDs and PCDFs, expressed in WHO-TEFs, pg/g fat), sum of dioxins and dioxin-like PCBs (sum of PCDDs, PCDFs and DL-PCBs, expressed in 2005 WHO-TEFs, pg/g fat) and sum of PCB28, PCB52, PCB101, PCB138, PCB153 and PCB180 (ICES-6) in ng/kg fat.

Table 3: Maximum levels for dioxins, furans and PCBs in food[1]

FOODSTUFFS	MAXIMUM LEVELS		
	Sum of dioxins and furans (WHO-PCDD/F-TEQ) [2]	Sum of dioxins, furans and dioxin-like PCBs (WHO-PCDD/F-PCB-TEQ) [2]	Sum of PCB28, PCB52, PCB101, PCB138, PCB153 and PCB180 (ICES-6) [2]
5.1 Meat and meat products (excluding edible offal) of the following animals [3] - bovine animals and sheep - poultry - pigs	2.5 pg/g fat[4] 1.75 pg/g fat [4] 1 pg/g fat [4]	4.0 pg/g fat[4] 3.0 pg/g fat[4] 1.25 pg/g fat[4]	40 ng/g fat[4] 40 ng/g fat[4] 40 ng/g fat[4]
5.2 Liver of terrestrial animals referred to in 5.1[3], and derived products thereof	4.5 pg/g fat[4]	10.0 pg/g fat[4]	40 ng/g fat[4]
5.3 Muscle meat of fish and fishery products and products thereof [5] [6], with the exemption of: - wild caught eel - wild caught fresh water fish, with the exception of diadromous fish species caught in fresh water - fish liver and derived products - marine oils The maximum level for crustaceans, applies to muscle meat from appendages and abdomen [7]. In case of crabs and crab-like crustaceans (*Brachyura* and *Anomura*), it applies to muscle meat from appendages.	3.5 pg/g wet weight	6.5 pg/g wet weight	75 ng/g wet weight
5.4 Muscle meat of wild caught fresh water fish with the exception of diadromous fish species caught in fresh water, and products thereof[5]	3.5 pg/g wet weight	6.5 pg/g wet weight	125 ng/g wet weight
5.5 Muscle meat of wild caught eel (*Anguilla anguilla)* and products thereof	3.5 pg/g wet weight	10.0 pg/g wet weight	300 ng/g wet weight
5.6 Fish liver and derived products thereof with the exception of marine oils referred to in point 5.7	-	20 pg/g wet weight[8]	200 ng/g wet weight[8]

5.7 Marine oils (fish body oil, fish liver oil and oils of other marine organisms intended for human consumption)	**1.75 pg/g fat**	**6.0 pg/g fat**	**200 ng/g fat**
5.8 Raw milk[3] and dairy products[3], including butter fat	**2.5 pg/g fat[4]**	**5.5 pg/g fat[4]**	**40 ng/g fat[4]**
5.9 Hen eggs and egg products[3]	**2.5 pg/g fat[4]**	**5.0 pg/g fat[4]**	**40 ng/g fat[4]**
5.10 Fat of the following animals **- bovine animals and sheep** **- poultry** **- pigs**	**2.5 pg/g fat** **1.75 pg/g fat** **1 pg/g fat**	**4.0 pg/g fat** **3.0 pg/g fat** **1.25 pg/g fat**	**40 ng/g fat** **40 ng/g fat** **40 ng/g fat**
5.11 Mixed animal fats	**1.5 pg/g fat**	**2.5 pg/g fat**	**40 ng/g fat**
5.12 Vegetable oils and fats	**0.75 pg/g fat**	**1.25 pg/g fat**	**40 ng/g fat**
5.13 Foods for infants and young children[9]	**0.1 pg/g wet weight**	**0.2 pg/g wet weight**	**1.0 ng/g wet weight**

(1) Dioxins (sum of polychlorinated dibenzo-para-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), expressed as World Health Organisation (WHO) toxic equivalent using the WHO-toxic equivalency factors (WHO- TEFs)) and sum of dioxins and dioxin-like PCBs (sum of PCDDs, PCDFs and polychlorinated biphenyls (PCBs), expressed as WHO toxic equivalent using the WHO-TEFs). WHO-TEFs for human risk assessment based on the conclusions of the World Health Organization (WHO) – International Programme on Chemical Safety (IPCS) expert meeting which was held in Geneva in June 2005 (Martin van den Berg *et al*., The 2005 World Health Organization Re-evaluation of Human and Mammalian Toxic Equivalency Factors for Dioxins and Dioxin-like Compounds. Toxicological Sciences 93(2), 223–241 (2006))

(2) Upperbound concentrations: Upperbound concentrations are calculated on the assumption that all of the values of the different congeners below the limit of quantification are equal to the limit of quantification.

(3) Foodstuffs listed in this category as defined in Regulation (EC) No 853/2004 of the European Parliament and of the Council of 29 April 2004 laying down specific hygiene rules for food of animal origin (OJ L 226, 25.6.2004, p. 22)

(4) The maximum levels are not applicable for food products containing < 1 % fat.

(5) Where fish are intended to be eaten whole, the maximum level applies to the whole fish.

(6) Foodstuffs listed in this category as defined in categories (a), (b), (c), (e) and (f) of the list in Article 1 of Regulation (EC) No 104/2000 (OJ L 17, 21.1.2000, p. 22) with the exclusion of fish liver referred to in point 5.11.

(7) This definition excludes the cephalothorax of crustaceans.

(8) In the case of canned fish liver, the maximum level applies to the whole edible content of the can.

(9) The maximum level refers to the products ready to use (marketed as such or after reconstitution as instructed by the manufacturer).

2.6 Brominated Flame Retardants

Brominated flame retardants (BFRs) are a group of chemicals which are added to many household products for the purpose of fire prevention. The types of products containing these chemicals include clothing and household textiles, furniture, computers and TVs.

There are 20-25 classes of BFRs that have been produced in the past or are currently in production, falling into at least three major classes: polybrominated diphenylethers (BDEs), hexabromocyclododecane (HBCDs, including three isomers) and tetrabromobisphenol A (TBBPA) and its derivatives. Other BFRs that have been used in the past or are still in use include the polybrominated phenols, decabromodiphenylethane and brominated phthalic acid derivatives. This survey of POPs in fish and fish products included BDEs, HBCDs, TBBPA, decabromodiphenylethane, hexabromobenzene and bis(2,4,6- tribromophenoxy)ethane.

The BFRs are classified as POPs, although they are less biopersistent than the dioxins and PCBs. Nevertheless, concern has been raised following the detection of BFRs in the environment, including in food and animal feed and in human tissues and fluids. There are however, limited data on their occurrence compared with dioxins and PCBs. For this reason, EFSA recommended in 2006 that a core group of BFRs including specific BDE congeners, HBCD and PBBs should be included in a European monitoring programme for feed and food[25]. EFSA additionally recommended the monitoring of BDE congeners outside the core group, decabromodiphenylethane, hexabromobenzene and bis(2,4,6- tribromophenoxy)ethane. In response to the EFSA recommendation, this survey of POPs in fish and fish products has included both the core and the additional BFRs recommended by EFSA.

2.6.1 Polybrominated diphenyl ethers

The term polybrominated diphenyl ethers (BDEs) refers to three commercial mixtures of decabromodiphenyl ether (decaBDE, DBDE), octabromodiphenyl ether (OctaBDE, OBDE), and pentabromodiphenyl ether (PentaBDE, pentaBDE). BDEs are similar in structure to PCBs (polychlorinated biphenyls) and also have some similarities to the dioxin family of chemicals. They contain the element bromine rather than the chlorine found in the PCBs. Like the dioxins and PCBs, BDEs break down slowly in the environment and continuous exposure can result in accumulation of BDEs in biota. Given the concerns regarding the persistence of these BFRs, including in food and animal feed and in human tissues, technical mixtures of both PentaBDE and OctaBDE were banned in the EU in 2004. In contrast to congeners present in PentaBDE (mainly BDE-47, BDE-99, BDE-100) and OctaBDE (mainly BDE-183) technical mixtures, it was considered at that stage that decaBDE (mainly BDE-209) did not meet the traditional criteria used to identify persistent, bioaccumulative and toxic (PBT) substances. However, there is increasing evidence as to its biopersistence and debromination to lower brominated congeners[26]. Use of DecaBDE has therefore been prohibited in electronics and electrical equipment since July 2006 under the Restriction of Hazardous Substances Directive (RoHS), and it has been recently listed by the European Chemicals Agency (ECHA) as a Substance of Very High Concern and hence as a candidate for authorised uses only under the European Parliament and Council Regulation 1907/2006 on Registration, Evaluation, Authorisation and Restriction of Chemical Substances (the REACH Regulation)[27].

Because BDEs have similarities to dioxins and PCBs, they may have some of the same effects on health as these chemicals, although they appear to be less toxic. Toxicological studies have shown that the main target organs for BDE toxicity are the liver, the thyroid and the reproductive and nervous system[28]. Some BDEs have endocrine or hormone disrupting properties, an effect that is also associated with dioxins and PCBs, and is thought to be associated with changes in fertility, sexual development and possibly certain types of cancer such as breast, testicular and prostate cancer[28]. It has also been reported that BDEs can have an effect on brain development in mice, slowing the learning process[28]. As with PCBs, exposure to BDEs may be particularly harmful during a critical window of brain development during pregnancy and early childhood. While the pentabromo compounds appear to be the most toxic, many of these persistent chemicals have not been extensively studied.

BDEs were first reported in wildlife species, including fish, seals, whales and birds' eggs. In the late 1990's they were reported in the breast milk of mothers in Sweden, and research showed that levels had increased from zero in 1970 to high levels in the 1990's in parallel with the use of BDEs. However, following restrictions on their use in Sweden, followed by the EU-wide ban on PentaBDE and Octa BDE mixtures, levels in breast milk in European women are now dropping.

The FSAI has carried out a number of studies on the occurrence of BDEs in Irish food[3,5,7]. A range of foodstuffs surveyed in 2005 showed a mean level for total BDE of 0.6 µg/kg fat in milk, 0.9 µg/kg fat in liver and levels ranging from 0.3 – 7.5 µg/kg in food supplements including fish oil supplements, which were at the higher end of the range. BDEs have been reported to be present in both farmed and wild salmon, including fish from Ireland[5,29,30,31], in Irish eels[32], and in other oily fish[5, 31]. The Marine Institute in Ireland measured BDEs in Irish farmed salmon in 2004 and found levels ranging from 2.28 to 4.61 (mean 3.05) µg/kg wet weight and 0.7 to 1.8 (mean 1.17) µg/kg wet weight for the sum of the 17 individual BDEs and for total HBCD respectively[33]. Similar levels were found in a more extensive survey carried out by the FSAI[5], confirming that levels of BDEs are generally higher in fish and fish products than in other foodstuffs.

There are no EU maximum limits for BDEs in food. Tolerable daily intakes (TDIs) have also not been derived, primarily due to limited toxicological data and the associated uncertainties with such studies[28]. EFSA has however, recently carried out a risk assessment of BDEs using a margin of exposure (MOE) approach with neurodevelopmental effects on behaviour as the critical endpoint[28]. Eight congeners were considered by EFSA to be of most concern/ interest: BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209. However, relevant toxicity data were only available for BDE-47, BDE-99, BDE-153 and BDE-209 and risk assessment could only be carried out for these four individual BDE congeners. EFSA noted that the highest source of exposure to BDEs was fish and other seafood, followed by meat and meat products, animal and vegetable fats and oils, milk and dairy products and eggs and egg products, which is in line with Irish data. EFSA concluded that current dietary exposure in the EU to BDE-47, BDE-153 and BDE-209 was not of concern, based on MOEs of larger than 2.5, the value which EFSA concluded might indicate that there is no health concern. However, as the MOEs for BDE-99 for young children (1-3 years) were only 1.4 and 0.7 for average and high consumers respectively, EFSA concluded that there is a potential health concern for this population group[28].

2.6.2 Hexabromocyclododecane (HBCDD)

Hexabromocyclododecane (HBCDD) has primarily been used to improve flame retardant characteristics of extruded and expanded polystyrene products. Technical HBCDD comprises three diasteroisomers (α, β and γ), with γ-HBCDD contributing approximately 80% to the technical

formulation. However, the α-isomer predominates in the environment and biota, and biomagnification is observed for the α-diastereoisomer with increasing trophic level in the food web, whereas γ-HBCDD is progressively diluted[34]. HBCDDs have been detected in a wide range of matrices including adipose tissue, liver and muscle and are of potential environmental and consumer food safety concern. Hence, the decision at EU level to phase out HBCDDs by mid-2015.

Isomer-specific HBCDD levels were analysed in fish samples landed/farmed in Ireland in 2004 and levels of total HBCD (sum of α-, β- and γ-HBCD) of 1.17 ± 0.26 µg/kg fresh weight in farmed salmon were in agreement with those of a previous Marine Institute survey[33]. Also, average levels for total HBCD observed in herring, salmon and mackerel samples were similar to those found in UK and Latvian surveys[30,35].

Toxicological studies have shown that the main target organs for HBCDD toxicity are the liver, the thyroid and the reproductive, nervous and immune system[36]. There are no EU maximum limits for HBCDDs in food. Tolerable daily intakes (TDIs) have also not been derived, primarily due to limited toxicological data and the associated uncertainties with such studies[36]. EFSA has however, recently carried out a risk assessment of HBCDDs using a margin of exposure (MOE) approach with neurodevelopmental effects on behaviour as the critical endpoint[36]. The highest source of exposure to HBCDDs was fish and other seafood, followed by meat and meat products, animal and vegetable fats and oils, milk and dairy products and eggs and egg products. EFSA concluded that current dietary exposure in the EU to HBCDDs was not of concern, based on MOEs of in the range of 700 to 3,000[36].

2.6.3 Polybrominated Biphenyls (PBBs)

The term polybrominated biphenyl (PBB) refers to a group of halogenated hydrocarbons, formed by substituting hydrogen by bromine in biphenyl. Theoretically, 209 congeners are possible, but only a few have been synthesized individually and characterised. PBBs are not known to occur as natural products. PBBs, manufactured for commercial use, consist mainly of hexa-, octa-, nona, and decabromobiphenyls, but also contain other homologues. PBBs were introduced as flame retardants in the early 1970s and were used mainly in small appliance and automotive applications, coatings, lacquers, and polyurethane foam.

The commercial product FireMaster(R) contained 60-80% of hexabromobiphenyl. After the Michigan disaster, when this compound was inadvertently added to animal feed instead of magnesium oxide and resulted in the destruction of thousands of cattle, pigs, and sheep, and millions of chickens, production was discontinued. In 2003, PBBs were listed as one of six controlled substances under the RoHS Directive, which restricts their use in electrical and electronic equipment.

Most of the PBB congeners are persistent, lipophilic and bioaccumulating, and they are thus found in biota, food and feed at low concentrations. Toxicological findings in animals include hepatic, renal, dermal/ocular, immunological, neurological, and developmental effects[37]. Other effects of exposure to PBBs include decreased thyroid function, body weight loss, and liver cancer. A number of PBBs are dioxin-like and bind to the Ah receptor, a mechanism of action which underlies many of the reported toxicological findings. Thus, inclusion of certain PBB congeners in the TEF scheme, e.g. PBB-77, PBB-126 and PBB-169 is considered appropriate[17]. EFSA recently carried out a risk assessment of PBBs using the hepatic carcinogenic effects as the critical effect, with a no-observed-effect level (NOEL) of 0.15 mg/kg body weight (b.w.)[37]. The intake of PBBs by

high and frequent consumers of fatty fish, the subgroup with the highest dietary exposure, was approximately six orders of magnitude less than this NOEL. Exposure for high consuming breast-fed infants was five orders of magnitude less. EFSA concluded therefore, that the risk to the European population from exposure to PBBs through the diet is of no concern[37].

2.6.4 Tetrabromo-Bisphenol A (TBBPA)

Commercial tetrabromo-bisphenol A (TBBPA) is the brominated flame retardant produced in the largest amounts globally. The demand for TBBPA and its derivatives accounts for over 60,000 tonnes per year. TBBPA is used as a reactive (primary use) or additive flame retardant in polymers, such as ABS, epoxy and polycarbonate resins, high impact polystyrene, phenolic resins, adhesives, and others. TBBPA is relatively less persistent and bio-accumulative than most of the other flame retardants, and the risk for the general population from TBBPA exposure has been previously considered insignificant[38]. However, since then, several papers have been published that would increase the level of concern regarding possible risks of TBBPA. Notably the papers of Van der Ven *et al*.[39] and Lilienthal *et al*.[40] have demonstrated an interaction with the thyroid hormone system in rats, mediated via its competitive binding to transthyretin (TTR) and resulting in decreased circulating thyroxin (T4) and increased triiodothyronine (T3). The dose at which the most sensitive of these effects was seen was 0.5 mg/kg bw/day, and the authors point out that the Margin of Exposure between this and predicted or actual measured levels for some human populations is low, additionally indicating concern for human health. EFSA has however, recently carried out a risk assessment of TBBPA, in which it identified that the main target for TBBPA toxicity is thyroid hormone homeostasis[41]. EFSA identified a confidence limit for a benchmark response of 10% (BMDL10) of 16 mg/kg b.w. reported for changes in thyroid hormone levels (decrease in circulating T4) as the critical reference point. Comparison of the “upper bound” dietary exposure estimate of 2.6 ng TBBPA /kg b.w. per day for the specific group of adult high fish consumers with the BMDL10 of 16 mg/kg b.w. resulted in an MOE of 6×10^6. EFSA concluded therefore, that the current dietary exposure to TBBPA does not raise a health concern[41].

2.6.5 Decabromodiphenylethane, Hexabromobenzene and Bis(2,4,6 tribromophenoxy)ethane

These compounds were included in the current study following a recommendation by EFSA in 2006 for inclusion in the core group of brominated flame retardants (BFRs) of a European monitoring programme for feed and food[25]. Very little is known regarding production volumes, occurrence in food and feed, persistence in the environment and toxicity of these compounds. In 2007, the European Commission conducted a review of production processes of decaBDE used in polymeric applications in electrical and electronic equipment and an assessment of the availability of potential alternatives to DecaBDE identified decabromodiphenylethane and bis(tribromophenoxy)ethane as two of 27 alternative substances.

Decabromodiphenylethane

Decabromodiphenylethane (DBDPE) has been used in recent years as a substitute for decaBDE in the manufacture of polymers for electronic and electrical applications, engineering resins and elastomers. DBDPE has been detected in household dust, sediment and in biota[42]. There have been a number of reports of DBDPE occurrence in fish and seafood[42], but in a recent survey undertaken by the FSAI on levels of a number of persistent organic pollutants including DPDPE in milk, carcass (animal) fat, eggs and liver produced in Ireland, no sample contained DBDPE levels above the LOD for the various foodstuffs surveyed[7]. EFSA has carried out a modelling exercise on a number of emerging BFRs including DBPDE and has concluded that while it was likely to persist

in the environment, its bioaccumulation potential was low, due to its large molecular mass (> 700)[42].

Toxicological data on DBPDE are limited. In a hazard assessment of DBDPE, EFSA has noted few adverse toxicological effects in two 90-day studies with the substance in rats other than (in one) an indication that DBDPE can alter thyroid hormone homeostasis (in parallel with other BFRs) and have possible effects on gene expression[42]. EFSA concluded however, that due to the very limited available information, either on occurrence or with respect to toxicological hazards, it was not possible to perform a risk characterisation for DBDPE or for a number of other emerging or novel BFRs.

Hexabromobenzene

Historically, hexabromobenzene (HBB) was a widely used BFR in Japan as an additive to paper, plastic and electronic goods. It is still in use today, albeit in much lower quantities[42,43]. It is reported not to be produced in Europe, however, it has been detected in ambient air, dust, sediment and biota in Europe as well as other parts of the world[42]. There have been a number of reports of HBB occurrence in fish[42], but in a recent survey undertaken by the FSAI on levels of a number of persistent organic pollutants including HBB in milk, carcass (animal) fat, eggs and liver produced in Ireland, no sample contained HBB levels above the LOD for the various foodstuffs surveyed[7]. EFSA has carried out a modelling exercise on a number of emerging BFRs including HBB and has concluded that its bioaccumulation potential is high[42]. In a hazard assessment of HBB, EFSA has noted some effect on the liver and enzyme activity in rodents but concluded however, that due to the very limited available information, it was not possible to perform a risk characterisation for HBB.

Bis(2,4,6-tribromophenoxy)ethane (BTBPE)

BTBPE, another alternative to octaBDE or decaBDE in polystyrene, thermoplastics and resins, has also been detected in ambient air, dust, sediment and biota in Europe as well as other parts of the world[41]. There have been reports of BTBPE occurrence in fish[42], but in a recent survey undertaken by the FSAI on levels of a number of persistent organic pollutants including BTBPE in milk, carcass (animal) fat, eggs and liver produced in Ireland, no sample contained BTBPE levels above the LOD for the various foodstuffs surveyed[7]. EFSA has carried out a modelling exercise on a number of emerging BFRs including BTBPE and has concluded that its bioaccumulation potential is high[42]. In a hazard assessment of BTBPE, EFSA noted that the substance was poorly absorbed but that no obvious adverse effects were seen in rats exposed in the diet at a concentration of 500 mg/kg, corresponding to 35 mg/kg b.w. for 14 days. Due to the very limited available information, EFSA concluded that it was not possible to perform a risk characterisation for BTBPE[42].

2.7 Legislation on Brominated Flame Retardants

There are currently no EU maximum limits for BFRs in food. As reflected in the recent hazard and risk assessments carried out by EFSA on these substances[28,36,37,41,42], tolerable daily intakes (TDIs) have not been derived for any BFRs, primarily due to the limited toxicological and exposure data available and the associated uncertainties in using such studies, and it is generally recognised that considerable work is required internationally on the toxicology and risk assessment of BFRs. However, as indicated in the information provided in previous sections on individual BFRs, regulatory controls or bans on the use of many of these substances have been introduced in the EU over the past decade due to their persistent and bioaccumulative properties and consequent concern regarding their effects on health and the environment.

2.8 Polybrominated Dibenzodioxins, Polybrominated Dibenzofurans and Mixed Halogenated Dibenzo-p-dioxins, Dibenzofurans and Biphenyls

Polybrominated dibenzo-p-dioxins (PBDDs), polybrominated dibenzofurans (PBDFs) and mixed halogenated dibenzo-p-dioxins (PXDDs) or dibenzofurans (PXDFs) dioxins/furans are not intentionally produced (except for scientific purposes) but are formed under the same conditions leading to the formation of PCDDs and PCDFs. They arise mainly as a result of combustion processes or exposure to high temperatures in the presence of oxygen, though in the presence of both bromine and chlorine sources[44,45]. Sources of halogens for the formation of PBDDs, PBDFs, PXDDs and PXDFs include BFRs, PCBs and PBBs[44]. PBDDs/PBDFs so far are not known to occur naturally, however a 2007 report suggests production of PBDDs by algae and/or cyanobacteria in the Baltic, which accumulate in the marine foodchain[46].

Theoretically, 75 PBDD and 135 PBDF chemical structures are possible. In addition, a large number of mixed halogenated congeners (1,550 brominated/chlorinated dibenzo- p-dioxins (PXDDs) and 3,050 brominated/chlorinated dibenzofurans (PXDFs) are theoretically possible. The most toxic congeners are those that are substituted at positions 2, 3, 7, and 8. There are seven 2,3,7,8-substituted PBDDs and ten 2,3,7,8-substituted PBDFs, as well as 337 possible 2,3,7,8-substituted PXDDs and 647 possible 2,3,7,8-substituted PXDFs[44].

Mixed polybrominated/chlorinated biphenyls (PXBs) are similarly not intentionally produced but are formed from halogenated precursors during thermal and chemical processes. A total of 9197 PXB congeners are theoretically possible. Given their structural similarity to the PCBs and PBBs, most attention has been paid to those congeners that can bind to the AhR receptor and hence have dioxin-like properties.

PBDDs/PBDFs have been found as contaminants in brominated organic chemicals, e.g. bromophenols and, in particular, in flame retardants, such as polybrominated diphenyl ethers (BDEs), decabromobiphenyl (decaBB or DBB), 1, 2-bis(tribromophenoxy)ethane, tetrabromobisphenol A (TBBPA), and others[44]. PBDFs and, to a lesser extent, PBDDs have also been detected as photochemical degradation products of brominated organic chemicals, such as BDEs and bromophenols[44].

In comparison to their chlorinated homologues, the PBDDs/PBDFs have higher molecular weights, higher melting points, lower vapour pressures, lower water solubility and a higher octanol-water partition coefficient (log K_{ow} values). Although the PBDDs/PBDFs/PXDDs/PXDFs/PXBs are more lipophilic and less water soluble than their chlorinated counterparts, they appear to be less environmentally persistent and more sensitive to UV degradation. The biochemical properties of the dioxins and furans are also altered by the bromine atom, since the larger size of the bromine atom alters susceptibility to enzymatic attack, and the carbon-bromine bond has lower strength than the carbon-chlorine bond[44].

All of these compounds have been detected in various environmental media including air, water, soil, sediments and biota[47] and in various foodstuffs[48]. In a recent survey undertaken by the FSAI on levels of a number of persistent organic pollutants in milk, carcass (animal) fat, eggs and liver produced in Ireland, PBDD/Fs were found in the majority of samples, the most frequently occurring congeners being 2,3,7,8-TBDF, 2,3,4,7,8-PBDF, 2,3,8-TBDF and 1,2,3,4,6,7,8-HpBDF7[7]. Similar results have been reported in other studies[49,50,51].

Little is known about the pharmacokinetic and pharmacodynamic properties of the PBDDs/PBDFs/ PXDDs /PXDFs/PXBs, and inferences are mostly drawn from the chlorinated analogs[52]. Essentially, all of the classic effects demonstrated for TCDD and the other chlorinated dioxins and furans, including lethality, wasting, thymic atrophy, teratogenesis, reproductive effects, chloracne, immunotoxicity, enzyme induction, decreases in T4 and Vitamin A, and increased hepatic porphyrins, have been observed in the limited toxicological studies available on the PBDDs/PBDFs[44,52]. The majority of PXDDs, PXDFs and PXBs tested are considered to have comparable or lower relative potencies than the corresponding PCDD, PCDFs and dioxin-like PCBs[53, 54]. Overall, the limited database on the health effects of these compounds supports the hypothesis that they have similar biological properties to their chlorinated relatives. Given the common mechanisms of action of a number of the congeners (binding to the AhR receptor) and effects, it is reasonable to predict that their presence will incrementally add to the total dioxin body burden[52]. Polybrominated dibenzo-p-dioxins and dibenzofurans and certain other individual and groups of compounds have been identified for possible future inclusion in the TEF concept, including 3,4,4'-TCB (PCB 37), mixed polyhalogenated dibenzo-p-dioxins and dibenzofurans, polyhalogenated naphthalenes, and polybrominated biphenyls[17]. However, more relative effect potency (REP) studies are needed before a TEF system for PBDD/Fs or PXDD/Fs can be established.

3. STUDY OUTLINE

The present study was undertaken to investigate the current levels of dioxins, furans, PCBs, BDEs, HBCDs, other brominated flame retardants, polybrominated dioxins, polybrominated furans, mixed halogenated dioxins/furans and mixed polybrominated/chlorinated biphenyls in fishery products available on the Irish market, and thereby increase the available data on the occurrence of these contaminants in Irish fish and fishery products.

3.1 Materials and Methods

For this survey, a total of 52 samples were prepared for analysis from fish and seafood collected in 2010, comprising the following species and retail groupings:

1. Fresh wild fish: albacore tuna, cod, haddock, hake, lemon sole, ling, mackerel, monkfish, plaice, ray, whiting
2. Farmed fish: Atlantic salmon, sea reared trout
3. Fresh crustaceans: prawns
4. Farmed shellfish (aquaculture): mussels

Unfortunately, it was not possible in the current survey to source wild salmon, due to unavailability, although similar studies carried out in 2001 and 2004 by the FSAI had focussed on comparison of these contaminants in farmed and wild salmon.

All fish were collected by staff of the Marine Institute from landings at Irish ports or production sites (farmed salmon, sea reared trout and mussels). Fresh albacore tuna samples were analysed individually, all other samples were composed of a number of pooled sub-samples (see Table 4). Capture locations were collected as appropriate.

Table 4: Details of fish, shellfish or crustacean sampled, numbers of pooled samples (N) and number of individual samples (sub-N) making up each pooled sample

Common Name	Species	N	sub-N	Origin	Details		
Cod	*Gadus morhua*	4	4, 10, 10, 44	Ireland	Wild cod	Raw	Skin off
Haddock	*Melanogrammus aeglefinus*	5	4, 10, 10, 10, 9	Ireland	Wild haddock	Raw	Skin off
Hake	*Merluccius merluccius*	1	5	Ireland	Wild hake	Raw	Skin off
Lemon sole	*Microstomus kitt*	4	7, 10, 13, 34	Ireland	Wild lemon sole	Raw	Skin off
Ling	*Molva molva*	2	3, 5	Ireland	Wild ling	Raw	Skin off
Mackerel	*Scomber scombrus*	5	11, 20, 21, 25, 30	Ireland	Wild mackerel	Raw	Skin off
Monkfish (white-bellied)	*Lophius piscatorius*	3	3, 10, 15	Ireland	Wild monk fish	Raw	Skin off
Monkfish (black-bellied)	*Lophius budegassa*	1	11	Ireland	Wild monk fish	Raw	Skin off
Mussels	*Mytilus edulis*	5	122-230	Ireland	Farmed (cultivated) mussels	Raw	Shelled
Plaice	*Pleuronectes platessa*	2	10, 29	Ireland	Wild plaice	Raw	Skin off
Prawns	*Nephrops norvegicus*	1	141	Ireland	Fresh prawns	Raw	Shelled
Ray	*Raja spp.*	1	10	Ireland	Wild ray	raw	Skin off
Salmon, Atlantic	*Salmo salar*	6	5, 5, 6, 5, 5	Ireland	Farmed salmon	Raw	Skin off
Sea reared trout	*Oncorhynchus mykiss**	2	5, 5	Ireland	Sea reared trout	Raw	Skin off
Tuna, Albacore	*Thunnus alunga*	5	1	Ireland	Wild tuna	Raw	Skin off
Whiting	*Merlangius merlangus*	5	7, 10, 10, 17, 35	Ireland	Wild whiting	Raw	Skin off

N = Number of pooled (individuals) analysed.
Sub-N = Number of individuals in a pooled sample
N.a. = Exact species information not available
* Also known as rainbow trout

Analysis of the samples was undertaken by the Food and Environment Research Agency, UK (FERA), York, UK during 2010 - 2011 under contract to the FSAI.

3.2 Analytes included in the Survey

3.2.1 Chlorinated compounds (PCDDs/PCDFs and PCBs)

PCDD/PCDF congeners

• 2,3,7,8-TCDD	• 2,3,7,8-TCDF
• 1,2,3,7,8-PeCDD	• 1,2,3,7,8-PeCDF
• 1,2,3,4,7,8-HxCDD	• 2,3,4,7,8-PeCDF
• 1,2,3,6,7,8-HxCDD	• 1,2,3,4,7,8-HxCDF
• 1,2,3,7,8,9-HxCDD	• 1,2,3,6,7,8-HxCDF
• 1,2,3,4,6,7,8-HpCDD	• 1,2,3,7,8,9-HxCDF
• 1,2,3,4,6,7,8,9-OCDD	• 2,3,4,6,7,8-HxCDF
	• 1,2,3,4,6,7,8-HpCDF
	• 1,2,3,4,7,8,9-HpCDF
	• 1,2,3,4,6,7,8,9-OCDF

PCB congeners

• PCB 77 (DL-PCB)	• PCB 153 (Marker PCB)	• PCB 110
• PCB 81 (DL-PCB)	• PCB 180 (Marker PCB)	• PCB 141
• PCB 126 (DL-PCB)	• PCB 18	• PCB 151
• PCB 169 (DL-PCB)	• PCB 31	• PCB 167
• PCB 105 (DL-PCB)	• PCB 33	• PCB 183
• PCB 114 (DL-PCB)	• PCB 37	• PCB 185
• PCB 123 (DL-PCB)	• PCB 41	• PCB 187
• PCB 156 (DL-PCB)	• PCB 44	• PCB 189
• PCB 157 (DL-PCB)	• PCB 47	• PCB 191
• PCB 167 (DL-PCB)	• PCB 49	• PCB 193
• PCB 189 (DL-PCB)	• PCB 51	• PCB 194
• PCB 118 (DL-PCB/ Marker PCB)	• PCB 60	• PCB 201
• PCB 28 (Marker PCB)	• PCB 66	• PCB 203
• PCB 52 (Marker PCB)	• PCB 74	• PCB 206
• PCB 101 (Marker PCB)	• PCB 87	• PCB 209
• PCB 138 (Marker PCB)	• PCB 99	

3.2.2 Brominated compounds (BDEs, BcCDDs/PCDFs and PCBs)

BDE congeners

- BDE-17
- BDE-28
- BDE-33
- BDE-37
- BDE-47
- BDE-49
- BDE-66
- BDE-71
- BDE-77
- BDE-85
- BDE-99
- BDE-100
- BDE-119
- BDE-126
- BDE138
- BDE153
- BDE 154
- BDE-155
- BDE-183
- BDE-197
- BDE-202
- BDE-203
- BDE-206
- BDE-207
- BDE-208
- BDE-209

HBCD Enantiomers

- Alpha-HBCD
- Beta-HBCD
- Gamma-HBCD

PBB congeners

- PBB 77 (3,3',4,4')
- PBB 126 (3,3',4,4',5)
- PBB 169 (3,3',4,4',5,5')
- PBB 15 (4,4')
- PBB 49 (2,2',4,5')
- PBB 52 (2,2',5,5')
- PBB 80 (3,3',5,5')
- PBB 101 (2,2',4,5,5')
- PBB 153 (2,2',4,4',5,5')
- PBB 209 (2,2',3,3',4,4',5,5',6,6')

PBDD/F congeners

- 2,3,7-TriBDD
- 2,3,7,8-TetraBDD
- 1,2,3,7,8-PentaBDD
- 1,2,3,4,7,8-/1,2,3,6,7,8-HexaBDD
- 1,2,3,7,8,9-HexaBDD
- 2,3,8-TriBDF
- 2,3,7,8-TetraBDF
- 1,2,3,7,8-PentaBDF
- 2,3,4,7,8-PentaBDF
- 1,2,3,4,7,8-HexaBDF
- 1,2,3,4,6,7,8-HeptaBDF

Other brominated flame retardants

- Decabromodiphenylethane
- Hexabromobenzene
- Bis(2,4,6-tribromophenoxyethane
- Tetrabromo-bisphenol A (TBBP-A)

Mixed halogenated dioxins and furans

• 2-B-7,8-CDD,	• 2-B-1,3,7,8-CDD	• 2-B-6,7,8-CDF
• 2-B-3,7,8-CDD	• 2-B-3,6,7,8,9-CDD	• 2,3-B-7,8-CDF
• 2,3-B-7,8-CDD	• 2-B-7,8-CDF	• 1-B-2,3,7,8-CDF
• 1-B-2,3,7,8-CDD	• 3-B-2,7,8-CDF	• 4-B-2,3,7,8-CDF
		• 1,3-B-2,7,8-CDF

Mixed halogenated biphenyls

• PXB105	• PXB126 di-Br
• PXB 118	• PXB126 tri-Br
• PXB126	• PXB 156

3.3 Methodology

Sample preparation

All samples were prepared in the Marine Institute. Skin was removed from all samples, subcutaneous lipid was removed from skin, added back to muscle samples and samples were aggregated as appropriate (see Table 4). Muscle tissue samples were then homogenised. Total extractable lipid content and moisture content were determined by the contracting analytical laboratory (FERA, UK). The homogenates of the samples were freeze-dried by the analytical laboratory (FERA, UK) and further homogenised by means of grinding.

Sample analysis

The analytical methodology for dioxin and PCB analysis followed EU Directive 2002/69/EC (laying down the methods of analysis for the determination of dioxin-like PCBs in foodstuffs), further guided by the analytical criteria given in Regulation 1883/2006. All analyses were carried out using ^{13}C -labelled internal standards and measurement was made using both high-resolution GC-MS and low-resolution GC-MS as appropriate (for ortho-substituted PCBs). Brominated dioxins (PBDD/Fs) BDEs and brominated biphenyl (PBB) analysis was carried out using similar methodology to that used for the chlorinated dioxins and PCBs – i.e. HRGC-HRMS and ^{13}C-labelled internal standardisation[55]. HBCD enantiomers and tetrabromo-bisphenol A were measured in acid-hydrolysed and purified sample extracts, by LC-MS/MS using ^{13}C-labelled internal standards[56]. Methodology for the other remaining three brominated compounds, hexabromobenzene, decabromodiphenylethane, and bis(246 tribromophenoxy)ethane was similar to that for chlorinated dioxins and PCBs. The samples were fortified with either ^{13}C hexabromobenzene, ^{13}C bis-(2,4,6-tribromophenoxy)ethane or ^{13}C decabromodiphenylethane, homogenised and extracted on a bed of modified silicas using a hexane:dichloromethane mixture. The extracts were concentrated, treated with acid and purified using florisil, before concentration to final volume and addition of the^{13}C labelled syringe standard. Analytes were then measured using high resolution gas chromatography/high resolution mass spectrometry and quantified using the ^{13}C-labelled internal standards.

4. RESULTS

4.1 Dioxins, Furans and PCBs

Table 5 presents summary information on the levels of PCDD/Fs, dioxin-like PCBs and indicator PCBs measured in the range of fish species, mussels and prawns sampled during this study.

Results are expressed as total 2005 WHO-TEQs in ng/kg wet (wet) weight for PCDD/Fs and dioxin-like PCBs separately and for the sum of PCDD/Fs and dioxin-like PCBs together, and as the sum total in µg/kg wet weight for the 6 indicator PCBs, PCBs 28, 52, 101, 138, 153 and 180. In each case, results are presented as upper-bound values, substituting values below the analytical limit of quantification with the limit of quantification (<LOQ=LOQ).

Table 5: Upper-bound levels (<LOQ = LOQ) of PCDD/Fs, DL-PCBS and total PCDD/Fs & DL-PCBS (2005 WHO TEQs, pg/g wet weight), and sum of 6 Indicator PCBs in fishery products (µg/kg wet weight)

Sample	N (sub-N)	Statistics	*ΣDL PCDD/F & PCBs*	*PCDD/F*	*DL- PCBs*	*6 Indicator PCBs*
			WHO TEQs pg/g wet weight			µg/kg
Cod, wild	4 (4, 10, 10, 44)	Mean	0.05	0.03	0.02	0.15
		Median	0.05	0.03	0.01	0.11
		Std. Dev	0.01	-	0.01	0.10
		Minimum	0.04	0.03	0.01	0.07
		Maximum	0.07	0.03	0.03	0.30
Haddock, wild	5 (4,10,10,10,9)	Mean	0.07	0.04	0.03	0.19
		Median	0.04	0.03	0.01	0.07
		Std. Dev	0.04	0.01	0.04	0.20
		Minimum	0.04	0.03	0.01	0.06
		Maximum	0.13	0.05	0.09	0.53
Hake, wild	1 (5)	N.A.	0.14	0.04	0.10	1.22
Lemon sole, wild	4 (7,10,13,34)	Mean	0.09	0.05	0.03	0.23
		Median	0.08	0.05	0.03	0.19
		Std. Dev	0.05	0.03	0.02	0.17
		Minimum	0.04	0.03	0.01	0.09
		Maximum	0.15	0.09	0.06	0.46

Sample	N (sub-N)	Statistics	*ΣDL PCDD/F & PCBs*	*PCDD/F*	*DL- PCBs*	*6 Indicator PCBs*
			WHO TEQs pg/g wet weight			µg/kg
Ling, wild	2 (3, 5)	Mean	0.06	0.03	0.03	0.25
		Median	0.06	0.03	0.03	0.25
		Std. Dev	-	-	-	-
		Minimum	0.05	0.03	0.04	0.27
		Maximum	0.07	0.03	0.02	0.33
Mackerel, wild	5 (11,20,21,25,30)	Mean	1.20	0.30	0.90	7.92
		Median	1.09	0.22	0.87	7.26
		Std. Dev	0.42	0.17	0.26	2.88
		Minimum	0.77	0.61	0.61	4.76
		Maximum	1.75	1.16	1.16	11.93
Monkfish, wild	4 (11,3,10,15)	Mean	0.05	0.03	0.02	0.16
		Median	0.04	0.03	0.01	0.09
		Std. Dev	0.02	0.00	0.01	0.15
		Minimum	0.04	0.03	0.02	0.07
		Maximum	0.07	0.03	0.04	0.39
Mussels, farmed	5 (122-230)	Mean	0.14	0.07	0.07	0.36
		Median	0.09	0.04	0.06	0.24
		Std. Dev	0.09	0.05	0.05	0.23
		Minimum	0.07	0.04	0.02	0.17
		Maximum	0.28	0.14	0.14	0.63
Plaice	2 (10, 29)	Mean	0.16	0.08	0.09	0.79
		Median	0.16	0.08	0.09	0.79
		Std. Dev	-	-	-	-
		Minimum	0.07	0.04	0.03	0.07
		Maximum	0.26	0.12	0.14	1.34
Prawns	1 (141)	N.A.	0.04	0.03	0.01	0.06
Ray	1 (10)	N.A.	0.05	0.03	0.02	0.13
Salmon, farmed Atlantic	6 (5-6)	Mean	1.47	0.35	1.12	11.11
		Median	1.45	0.36	1.09	11.28
		Std. Dev	0.55	0.12	0.43	4.06
		Minimum	0.57	0.13	0.44	4.39
		Maximum	2.11	0.49	1.62	16.03

Sample	N (sub-N)	Statistics	*ΣDL PCDD/F & PCBs*	*PCDD/F*	*DL- PCBs*	*6 Indicator PCBs*
			WHO TEQs pg/g wet weight			**µg/kg**
Sea reared trout	2 (5, 5)	Mean	0.84	0.21	0.63	6.24
		Median	0.84	0.21	0.63	6.24
		Std. Dev	-	-	-	-
		Minimum	0.51	0.12	0.38	3.70
		Maximum	1.17	0.30	0.87	8.77
Tuna, wild (albacore)	5 (1)	Mean	0.39	0.06	0.32	3.79
		Median	0.38	0.06	0.32	3.52
		Std. Dev.	0.04	0.01	0.04	0.46
		Minimum	0.33	0.06	0.27	3.42
		Maximum	0.44	0.07	0.36	4.50
Whiting, wild	5 (7,10,10,17,35)	Mean	0.14	0.05	0.09	0.75
		Median	0.13	0.04	0.09	0.72
		Std. Dev.	0.11	0.02	0.09	0.54
		Minimum	0.04	0.03	0.01	0.15
		Maximum	0.29	0.07	0.22	1.73

N = Number of pooled (individuals) analysed.
Sub-N = Number of individuals in a pooled sample.
N.A. = Not applicable

As reported in Table 5, the highest level of total TEQ (sum PCDD/F & DL-PCB) was observed in farmed salmon, at a mean concentration of 1.47 pg/g wet weight, followed by mackerel with a mean TEQ level (sum PCDD/F & DL-PCB) concentration of 1.20 pg/g wet weight and sea reared trout with a mean TEQ level of 0.84 pg/g wet weight. It is notable that these three species are oily fish, while with the exception of tuna, all other species surveyed in this study were non-oily white fish. The tuna samples analysed in the study had a mean TEQ level of 0.39 pg/g wet weight, while total TEQ for the non-oily white fish surveyed ranged from 0.05 pg/g wet weight (cod, monkfish and ray) to 0.14 – 0.16 pg/g wet weight (whiting and plaice). As can be seen from Table 5, DL-PCBs were the major contributors to the total TEQ for the three species salmon, mackerel and sea reared trout (present at approximately three to four times the levels found for the PCDD/Fs), with an even higher ratio between DL-PCBs and PCDD/Fs being found in tuna. The levels of PCDD/Fs found in tuna were generally similar to those found in the non-oily white fish, and as already indicated the total TEQ in tuna was considerably lower than in salmon, mackerel and sea reared trout.

It should be noted that the levels of PCDD/Fs and the sum of PCDD/Fs plus DL-PCBs, expressed as WHO TEQ, in all fish analysed in this survey were well below the legislative maximum limits for these contaminants, as shown in Table 3. The data are also presented in graphical form in Figure 1 for PCDD/Fs and DL-PCBs separately, while Figure 2 provides an overview of mean concentrations of indicator PCBs in the fish species covered by this survey.

Figure 1: Mean upper-bound WHO TEQ PCDD/F & DL-PCB pg/g wet weight in different fish species

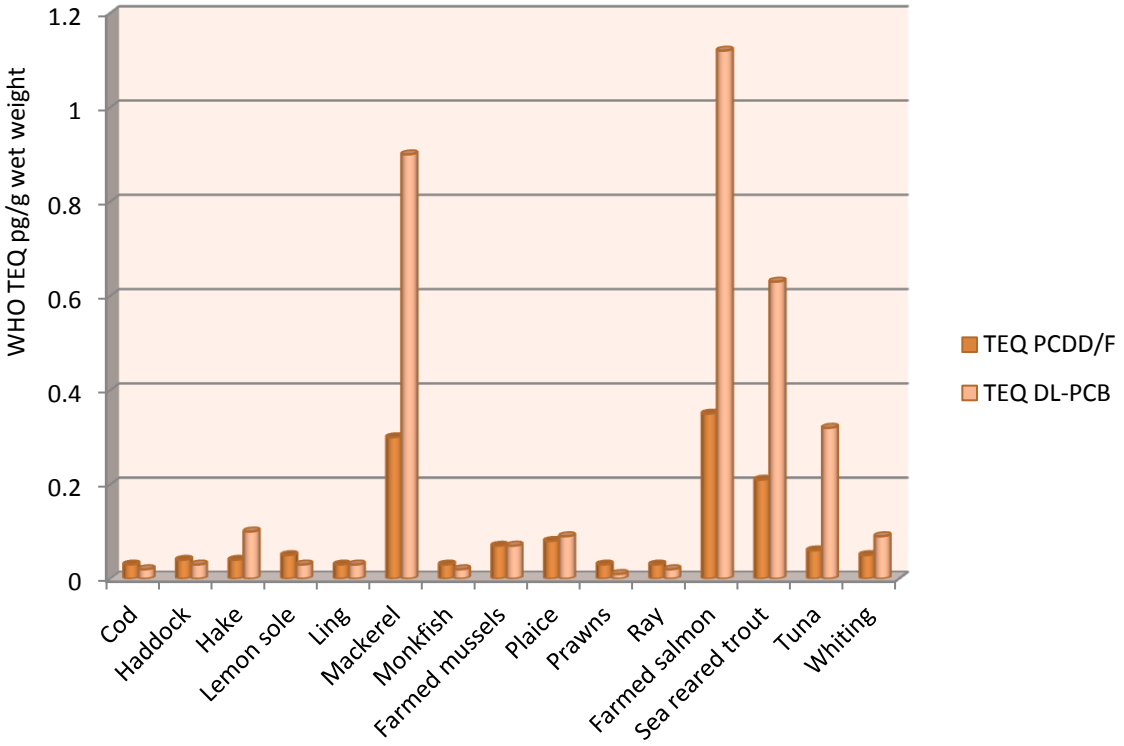
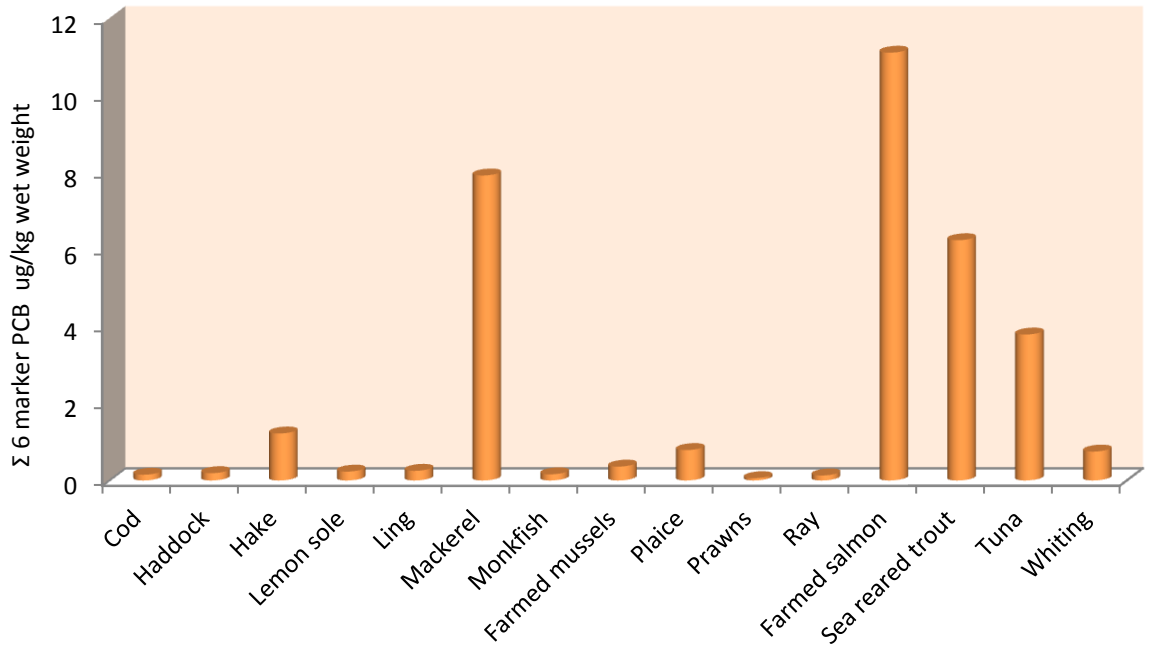


Figure 2: Mean concentration of Σ6 Indicator PCBs (µg/kg fresh weight, upper-bound)



Levels of lipophilic contaminants such as the PCDDs/PCDFs and PCBs are generally recognised to increase in fish species as the lipid content of the sample increases, supporting the contention that oily fish tend to accumulate such contaminants to a higher degree than non-oily fish. Table 6 summarises the mean lipid data for all the species groupings covered in this survey, as determined by the contractor (FERA, UK).

Table 6: Mean extractable lipid levels (%) determined in fish species in this survey

Fish Product	Average Lipid (%) ± SD	Range (%)
Cod	0.52 ± 0.13	(0.35 – 0.65)
Haddock	0.55 ± 0.15	(0.37 – 0.72)
Hake	1.55	-
Lemon sole	1.01 ± 0.30	(0.60 – 1.55)
Ling	0.46	(0.42 – 0.51)
Mackerel	14.53 ± 3.45	(9.35 – 19.0)
Monkfish	0.52 ± 0.13	(0.36 – 0.41)
Mussels	1.57 ± 0.36	(1.22 – 2.13)
Plaice	1.09	(0.66 – 1.52)
Prawns	0.85	-
Ray	0.68	-
Salmon, farmed	13.6 ± 3.79	(7.45 – 17.6)
Sea reared trout	15.71	(8.99 – 22.42)
Tuna, albacore	7.06 ± 1.63	(4.46 – 8.53)
Whiting	0.73 ± 0.31	(0.37 – 1.11)

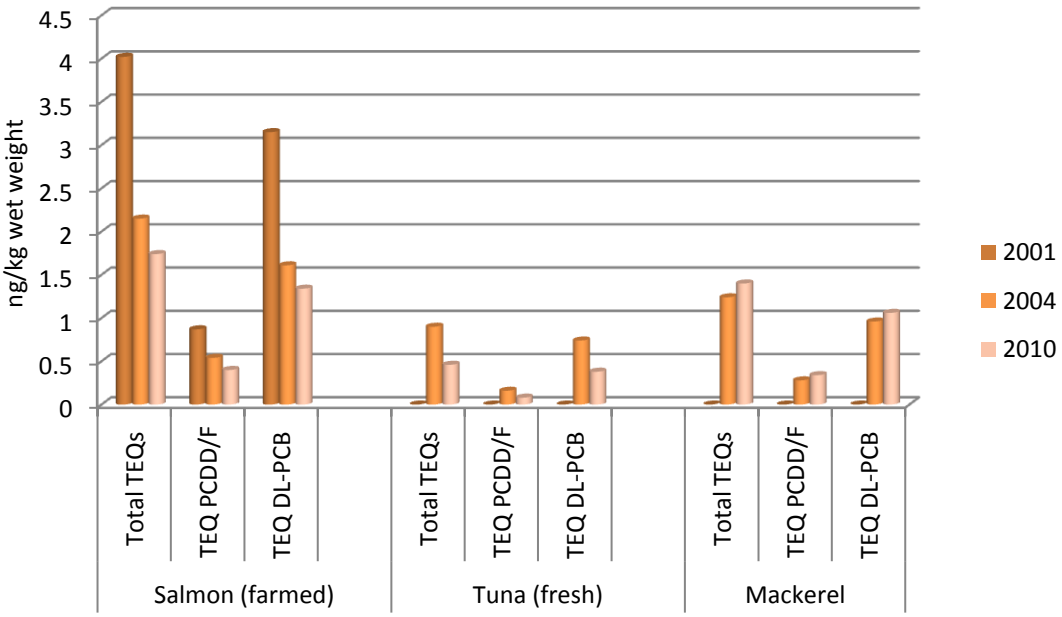
SD =standard deviation

The levels of dioxins and DL-PCBs measured in farmed salmon, fresh tuna and fresh mackerel[2] in this study can be compared with results obtained in the earlier studies carried out by the FSAI in 2001 and 2004 (FSAI, 2002; Tlustos *et al.,* 2007), while being mindful of the fact that direct comparisons are complicated by the differences in the analytical limits of detection between the surveys, and the analysis in the 2001 survey was carried out by a different laboratory.

The results of the comparison are shown in Figure 3, the levels shown being expressed in 1998 WHO-TEQs rather than 2005 TEQs, since all results in the 2001 and 2004 surveys had been expressed as 1998 TEQs.

[2] Data were only available for farmed salmon at all three time points. No data were available for fresh tuna and mackerel for the 2001 survey.

Figure 3: Comparison of levels of PCDD/Fs, DL-PCBS and total PCDD/Fs & DL-PCBs (ng/kg wet weight) in farmed salmon, mackerel and tuna sampled in 2001, 2004 and 2010



As evident in Figure 3, this comparison revealed a marked decline in the levels of dioxins and DL-PCBs, expressed as 1998 WHO TEQs, in farmed salmon over the nine-year period, the total TEQs in the fish sampled in 2010 being 1.74 ng WHO TEQs/kg wet weight of fish, compared with 4.02 ng/kg wet weight in 2001. Similar decreases were seen in PCDD/Fs alone (from 0.87 ng WHO TEQs/kg wet weight of fish to 0.4 ng/kg wet weight) and in DL-PCBs (from 3.15 ng WHO TEQs/kg wet weight of fish to 1.34 ng/kg wet weight). As already indicated in Table 5, in 2010, DL-PCBs were the major contributors to the total TEQ for the three species, and this was also the case in 2004. A decline in total WHO TEQ was evident in tuna between 2004 and 2010, but in mackerel, the total TEQ showed very little change over the same period. It should be noted that this consumer-focused surveillance sampling programme was not designed to detect temporal trends so inferences about general changes in environmental concentrations should be avoided. Other factors not controlled for in this programme, such as location, fish stock, migration patterns, and biological/physiological factors, influence contaminant burdens, and can confound quantitative trend detection.

4.2 Brominated Flame Retardants

4.2.1 BDEs

Of the 26 BDE congeners analysed, only 6 congeners (BDEs 47, 49, 99, 100, 154 and 155) were found in notable quantities in some to all of the species surveyed. BDEs 37, 71, 126, 138 and 203 were not detected in any sample above the Limit of Quantification (LOQ) of 0.002 µg/kg wet (wet) weight, while BDEs 17, 28/33, 66, 77, 85, 119,153, 183, 197, 202, 206, 207, 208 and 209 were found in low to very low concentrations in certain species only (primarily mackerel, mussels, salmon, sea reared trout and tuna).Table 7 presents an overview of the percentage of the individual BDEs quantified in all 53 samples analysed.

Table 7: Overview of BDE congener occurrence above the quantifiable level in fish species covered in this survey

BDE No	No Samples* >LOQ	Species	%
47	51	All	96.2
49, 99, 100, 154, 155	40	Mostly in haddock, hake, lemon sole, ling, mackerel, farmed mussels, farmed salmon, sea reared trout, tuna, whiting	75.5
17, 28/33, 66, 77, 85, 119,153	26	Mostly in mackerel, farmed mussels, farmed salmon, sea reared trout and tuna	81.4
183, 197, 202, 206, 207, 208	17	Mostly in mackerel, farmed mussels, farmed salmon, sea reared trout and tuna	42.9
209	10	Mostly in mackerel, farmed mussels, farmed salmon, sea reared trout and tuna	25.7
37, 71, 126, 138, 203	0	Not quantified in any sample	0

*From total of 52 samples

Table 8 presents the sum of the mean levels of all those BDE congeners detected in any species, substituting values below the analytical limit of quantification with the limit of quantification (<LOQ=LOQ) in those samples in which the relevant BDE was not detected. Table 8 also contains the mean content of the six predominant BDEs, BDEs 47, 49, 99, 100, 154 and 155, found in significant quantities in the majority of species analysed.

Table 8: Mean upper-bound levels (<LOQ = LOQ) of Σ26 BDEs in fish species covered in this survey (µg/kg wet weight)

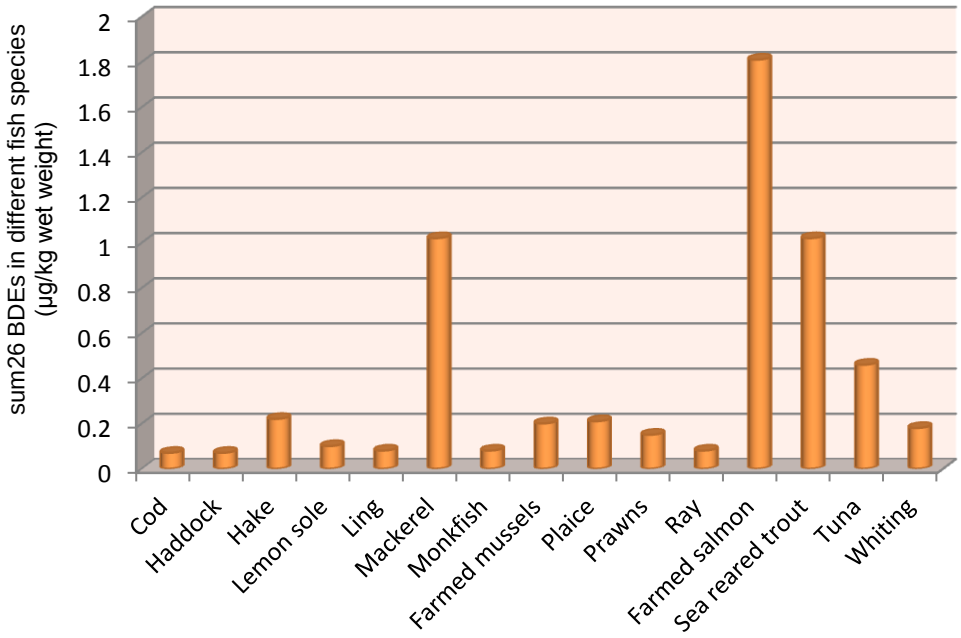
Sample	N (subN)	Σ BDE	BDE 47	BDE 49	BDE 99	BDE 100	BDE 154	BDE 155
		µg/kg wet weight						
Cod, wild	4 (4, 10, 10, 44)	0.07	0.007	0.002	0.002	0.003	0.002	0.002
Haddock, wild	5 (4, 10, 10, 10, 9)	0.07	0.009	0.001	0.003	0.004	0.003	0.004
Hake, wild	1 (5)	0.22	0.084	0.030	0.007	0.022	0.015	0.022
Lemon sole, wild	4 (7, 10, 13, 34)	0.10	0.014	0.004	0.003	0.006	0.006	0.008
Ling, wild	2 (3, 5)	0.08	0.016	0.003	0.002	0.005	0.003	0.005
Mackerel, wild	5 (11, 20, 21, 25, 30)	1.02	0.37	0.13	0.11	0.11	0.07	0.06
Monkfish, wild	4 (11, 3, 10, 15)	0.08	0.005	0.002	0.002	0.003	0.002	0.003
Mussels, farmed	5 (122-230)	0.2	0.057	0.025	0.022	0.022	0.004	0.005
Plaice	2 (10, 29)	0.21	0.059	0.011	0.003	0.020	0.021	0.033
Prawns	1 (141)	0.15	0.002	0.002	0.002	0.002	0.002	0.002
Ray	1 (10)	0.07	0.008	0.002	0.002	0.002	0.002	0.003
Salmon, farmed Atlantic	6 (5-6)	1.81	0.790	0.177	0.173	0.194	0.147	0.097
Sea reared trout	2 (5, 5)	1.02	0.434	0.131	0.094	0.105	0.062	0.046
Tuna, albacore	5 (1)	0.46	0.190	0.048	0.017	0.044	0.044	0.032
Whiting, wild	5 (7, 10, 10, 17, 35)	0.18	0.053	0.015	0.004	0.015	0.009	0.023

N = Number of pooled (individuals) analysed.
Sub-N = Number of individuals in a pooled sample.

As can be seen from Table 8, the highest concentrations of total BDE (Σ26 congeners) were observed in farmed Atlantic salmon (1.81 µg/kg wet weight), followed by mackerel and sea reared trout (1.02 µg/kg wet weight in both species) and fresh tuna (0.46 µg/kg wet weight). Non-oily white fish, mussels and prawns had lower levels, although there was some variation between the

species. The result for the single pooled sample of prawns was notable for the fact that the only BDE detected in this species was BDE 209, at a level of 0.1 µg/kg wet weight, which was the highest concentration of this congener detected in any sample in the study. The data are also presented in graphical form in Figure 4 below.

Figure 4: Mean upperbound concentration of sum 26 BDE in fish species covered in this survey (µg/kg wet weight)



Comparison of the sum of the 26 BDE congeners measured in various species in this study with the sum of 16 BDEs measured in the study carried out by the FSAI in 2004[4] is not totally appropriate, given the different number of BDEs measured in the two studies, and in particular, the different LOQs applicable in the two studies. The study carried out in 2004 had higher LOQs, leading to higher upperbound values for the individual BDEs. The mean sum (upperbound) of 16 BDEs in farmed salmon in 2004 was 3.71 µg/kg wet weight, while the value for fresh tuna was 0.96 µg/kg wet weight and that for mackerel was 1.35 µg/kg wet weight. As can be seen from Table 8, these levels are appreciably higher than those measured in the current study, particularly for farmed salmon. While the difference in the results between the two studies is likely in part to be due to the LOQ issue as referred to above, the lower levels seen in the current study, together with the fact that more BDEs were measured, probably indicate a decline in the environmental burden of BDEs over the period.

4.2.2 HBCD

Total and isomer specific HBCD levels measured in this study are presented in Table 9. α-HBCD was the predominant isomer detected; the β- and γ-isomers were generally below the LOQ or were only found in trace amounts. α-HBCD was detected above the LOQ in all samples of mackerel, salmon, sea reared trout, tuna and mussels analysed, and was also detected in one or more samples of the other species tested in this study, although levels in cod, lemon sole, ling, plaice, prawns and ray were at the LOQ or were indicative at best. β- HBCD was detected in trace amounts in mackerel, mussels and farmed salmon only, while γ-HBCD was detected in mackerel and farmed salmon at slightly higher but still trace amounts. Levels of total HBCD (sum of α-, β- and γ-HBCD) in farmed salmon of 0.55 ± 0.2 µg/kg fresh weight were lower than those found in the 2004 FSAI survey[4], which reported levels of 1.17 ± 0.26 µg/kg fresh weight. However, as with the sum total of BDEs reported in the previous section, these results are not directly comparable, given the different LOQs applicable in the two studies.

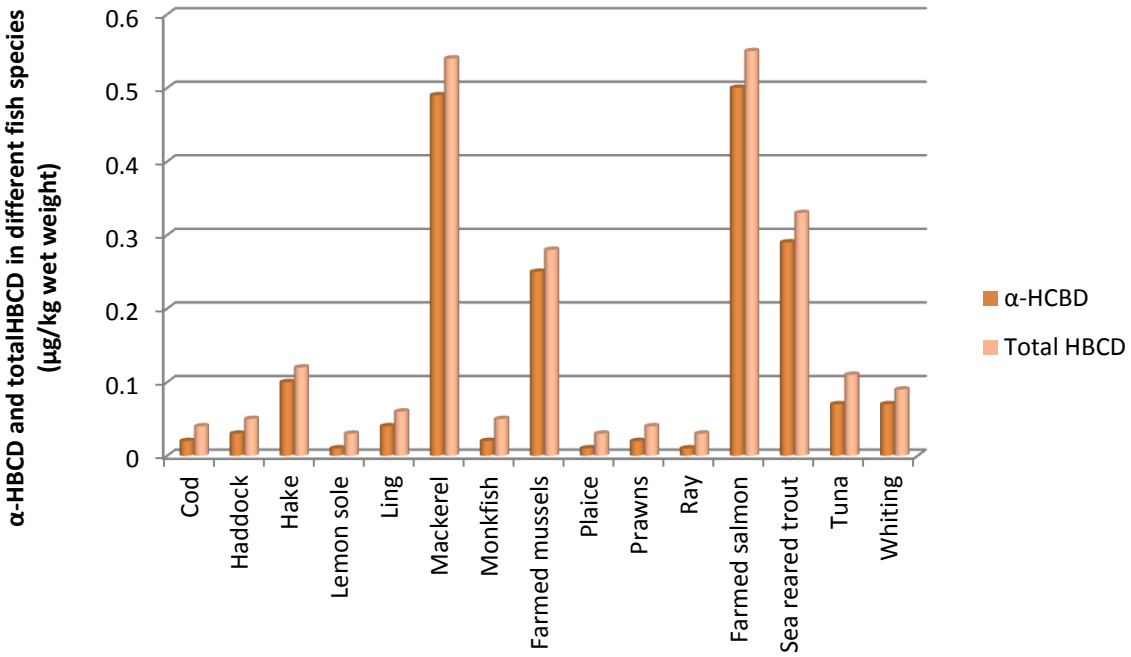
Table 9: Levels of α, β and γ-HBCD isomers and total (upperbound) HBCD in fish species covered in this study (µg/kg wet weight)

Species	αHBCD (mean ± SD)	βHBCD (mean ± SD)	γHBCD (mean ± SD)	Total
Cod	0.02 ± 0.01	0.01 ± 0.00	0.01 ± 0.005	0.04
Haddock	0.03 ± 0.02	0.01 ± 0.00	0.01 ± 0.00	0.05
Hake	0.1	0.01	0.01	0.12
Lemon sole	0.01 ± 0.01	0.01 ± 0.00	0.01 ± 0.00	0.03
Ling	0.04	0.01	0.01	0.06
Mackerel	0.49 ± 0.32	0.02 ± 0.01	0.03 ± 0.02	0.54
Monkfish	0.02 ± 0.01	0.01 ± 0.00	0.02 ± 0.02	0.05
Farmed mussels	0.25 ± 0.19	0.02 ± 0.00	0.01 ± 0.00	0.28
Plaice	0.01	0.01	0.01	0.03
Prawns	0.02	0.01	0.01	0.04
Ray	0.01	0.01	0.01	0.03
Farmed salmon	0.5 ± 0.19	0.02 ± 0.01	0.03 ± 0.02	0.55
Sea reared trout	0.29	0.02	0.02	0.33
Tuna (albacore)	0.07 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.11
Whiting	0.07 ± 0.01	0.01 ± 0.00	0.01 ± 0.01	0.09

SD = standard deviation

The data for HBCD are also presented in graphical form in Figure 5 below, for α-HBCD and total HBCD only.

Figure 5: Mean upperbound concentration of α-HBCD and total HBCD in fish species covered in this survey (µg/kg wet weight)



4.2.3 Polybrominated Biphenyls (PBBs)

Trace levels of PBBs were detected in certain species, mainly the oily fish. PBB-77, which binds to the Ah receptor and may therefore have dioxin-like properties, was found in all samples of mackerel, farmed mussels, farmed salmon and sea reared trout analysed and in one of the two plaice samples. Table 10 shows the levels measured in these five species, on a ng/kg wet weight basis. Very low levels were also identified in one ling and one haddock sample and also in a number of samples of the non-oily fish, namely in haddock (three of the four samples tested), ling (both samples), plaice (both samples), prawns (single sample only), tuna (two of the five samples tested), lemon sole (two of the four samples tested) and whiting (three of the five samples tested. PBB-126 and PBB-169, which also bind to the Ah receptor, were not detected in any sample tested, other than one sample of plaice in which the concentration of PBB-126 was at the LOQ. Of the other (non-dioxin-like) PBBs measured in this survey (the measured congeners were PBB-15, PBB-49, PBB-52, PBB-80, PBB-101, PBB-153 and PBB-209) PBB-15, PBB-80 and PBB-209 were not detected in any sample. The other congeners were all detected in the oily fish species, mackerel, farmed salmon, sea reared trout and tuna but, unlike PBB-77, not in mussels. PBB-52 was present at slightly higher levels and in more samples than PBB-49, PBB-101 and PBB-153. Results for all four congeners in mackerel, farmed salmon, sea reared trout and tuna are shown in Table 10.

Table 10: Levels of PBB-77, PBB-49, PBB-52, PBB-101 and PB-153 in mackerel, mussels, plaice, farmed salmon and sea reared trout (ng/kg wet weight, upperbound)

Species	PBB-77 (mean ± SD)	PBB-49 (mean ± SD)	PBB-52 (mean ± SD)	PBB-101 (mean ± SD)	PBB-153 (mean ± SD)
Mackerel	0.019 ± 0.007	2.4 ± 0.5	4.0 ± 1.9	2.0 ± 0.0	ND
Farmed mussels	0.008 ± 0.002	ND	ND	ND	ND
Plaice	0.008 ± 0.004	ND	ND	ND	ND
Farmed salmon	0.021 ± 0.006	4.5 ± 1.5	8.0 ± 3.6	3.7 ± 1.6	3.8 ± 1.5
Sea reared trout	0.021 ± 0.009	2.5 ± 0.7	4.5 ± 2.1	2.5 ± 0.7	2.0 ± 0.0
Tuna (albacore)	ND	2.0 ± 0.0	2.0 ± 0.0	2.6 ± 0.5	2.2 ± 0.4

SD = Standard deviation
ND = Not detected above LOQ

4.2.4 Other brominated flame retardants

This survey has also included tetrabromo-bisphenol A (TBBPA) and the three compounds decabromodiphenylethane (DBDPE), hexabromobenzene (HBB) and bis(2,4,6 tribromophenoxy)ethane (BTBPE), recommended by EFSA for inclusion in any monitoring programme for the brominated flame retardants. TBBPA and HBB were not detected in any sample at levels above the LOQ, while BTBPE was detected at the LOQ (0.01 µg/kg) in one sample of mussels and at a level of 0.01 µg/kg in a sea reared trout sample. DBDPE was detected in two monkfish samples and a whiting sample, again at levels around the LOQ.

4.2.5 Polybrominated dibenzodioxins, polybrominated dibenzofurans and mixed halogenated dibenzo-p-dioxins, dibenzofurans and biphenyls

A range of PBDDs, PBDFs, mixed halogenated dioxins and furans and mixed halogenated biphenyls were measured in this study as shown in Section 3.2.2.

The PBDDs and PBDFs are considered to be dioxin-like and the TEFs assigned to the fully chlorinated PCDDs and PCDFs can be used to derive a TEQ for samples containing the brominated compounds. The most commonly detected brominated congener, detected in one or more samples from every species investigated in this study, was 1,2,3,4,6,7,8-HeptabromoBDF (Table 11). For the majority of species, this was the only brominated congener detected. It was notable however that mussels, and to a lesser extent, farmed salmon and sea reared trout, contained measurable levels of the other brominated congeners. As shown in Table 11, the PBDFs predominated, with mussels containing 2,3,7-TriBDD, 2,3,8-TriBDF, 2,3,7,8-TetraBDF, 1,2,3,7,8-PentaBDF and 2,3,4,7,8-PentaBDF as well as 1,2,3,4,6,7,8-HeptabromoBDF. These congeners were also detected in farmed salmon and sea reared trout, with the exception of 2,3,7-TriBDD and 1,2,3,7,8-PentaBDF, but there were only very isolated findings of any of these congeners in other species, with the exception of 1,2,3,4,6,7,8-HeptabromoBDF. Interestingly, mackerel, which have been found to have comparatively high levels of the other brominated flame retardants surveyed in this study, were only found to contain trace amounts (at the LOQ) of 2,3,7,8-TetraBDF (one out of five samples), 2,3,4,7,8-PentaBDF (two out of five samples) and 1,2,3,4,6,7,8-HeptabromoBDF (one out of five samples), while tuna contained only 1,2,3,4,6,7,8-HeptabromoBDF (four out of five samples) and a trace amount of 2,3,4,7,8-PentaBDF (in one out of five samples).

Table 11: Levels of 2,3,7-TriBDD, 2,3,8-TriBDF, 2,3,7,8-TetraBDF,1,2,3,7,8-PentaBDF, 2,3,4,7,8-PentaBDF and 1,2,3,4,6,7,8-HeptabromoBDF in fish species covered in this survey (ng/kg wet weight)

Sample	2,3,7-TriBDD (mean ± SD)	2,3,8-TriBDF (mean ± SD)	2,3,7,8-TetraBDF (mean ± SD)	1,2,3,7,8-PentaBDF (mean ± SD)	2,3,4,7,8-PentaBDF (mean ± SD)	1,2,3,4,6,7,8-Heptabromo BDF (mean ± SD*)
Cod, wild	ND**	ND	ND	ND	ND	0.018 ± 0.006
Haddock, wild	ND	ND	ND	ND	ND	0.022 ± 0.007
Hake, wild	ND	ND	ND	ND	ND	0.018
Lemon sole, wild	ND	ND	ND	ND	ND**	0.015 ± 0.005
Ling, wild	ND	ND	ND	ND	ND	0.014
Mackerel, wild	ND	ND	ND**	ND	0.007 ± 0.004	0.016 ± 0.002
Monkfish, wild	ND	ND	ND	ND	ND	0.009 ± 0.003
Mussels, farmed	0.23 ± 0.16	0.054 ± 0.018	0.012 ± 0.006	0.006 ± 0.003	0.013 ± 0.007	0.036 ± 0.039
Plaice	ND	ND	ND	ND**	ND**	0.019
Prawns	ND	ND	ND	ND	ND	0.062
Ray	ND	ND	ND	ND	ND	ND
Salmon, farmed Atlantic	ND	0.008 ± 0.003	0.008 ± 0.003	ND	0.009 ± 0.003	0.048 ± 0.014
Sea reared trout	ND	ND	0.006	ND	0.011	0.030
Tuna, albacore	ND	ND	ND	ND	ND**	0.021 ± 0.004
Whiting, wild	ND	ND	ND	ND	0.005 ± 0.000	0.017 ± 0.002

ND = Not detected above LOQ
ND** = A trace in one sample only, just above the LOQ
*SD not reported when only 1-2 samples were analysed

The mean derived upperbound WHO TEQ attributable to PBBDs, and PBBFs for the majority of species surveyed in the study was 0.015 pg/g wet weight (worst case/LOQ value), the value for mussels was 0.020 ± 0.003, for salmon 0.020 ± 0.002 and for sea reared trout 0.022 ± 0.006.

Of the mixed halogenated dioxins and furans measured, only 2-B-7,8-CDD and 2-B-7,8-CDF were found in any sample above the LOQ, and only in mussels (apart from a trace quantity of 2-B-7,8-CDF in one out of five mackerel samples). Four of the six mixed halogenated biphenyls (PXBs) measured in the study, PXB 105, PXB 118, PXB 126 and PXB 156, were however, found in mackerel, salmon, sea reared trout and tuna and occasionally in trace amounts in one or more samples of the other species investigated in the study; PXB126 di-Br and PXB126 tri-Br were not detected above the LOQ in any species. The data obtained for those mixed halogenated dioxins, furans and biphenyls detected above the LOQ in any species are shown in Table 12, and

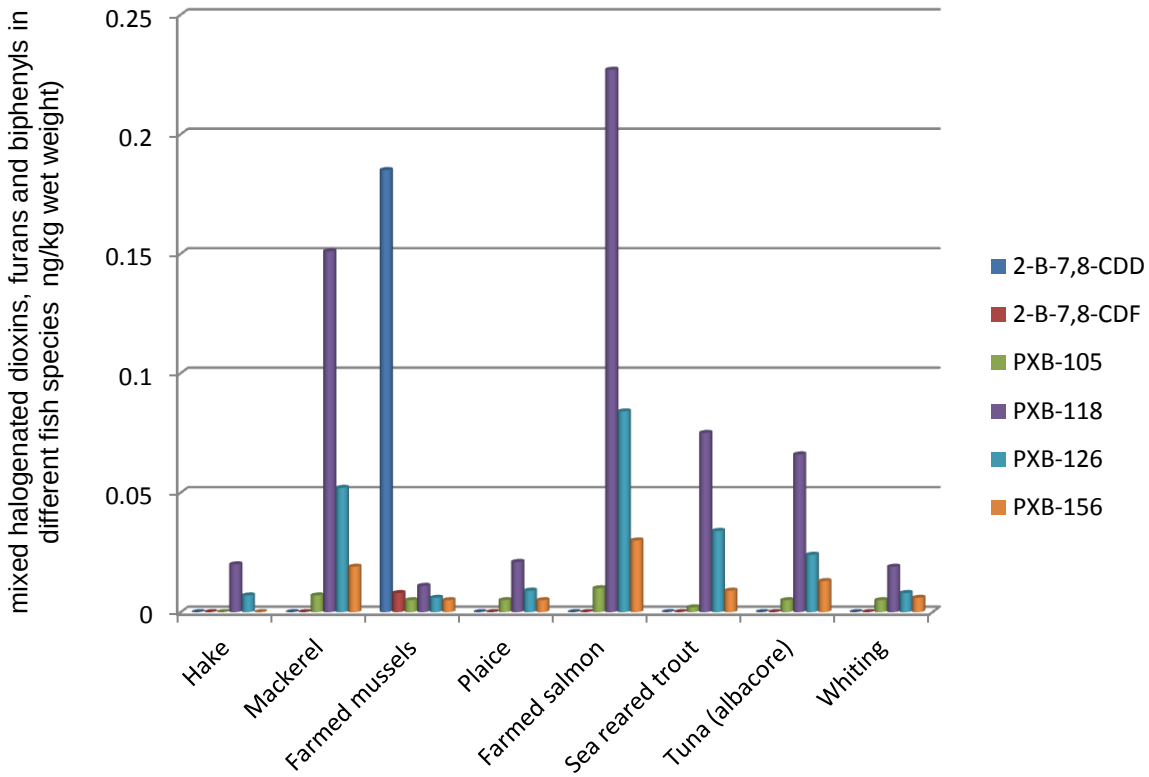
graphically in Figure 6. Data for cod (no values above the LOQ), haddock, lemon sole (trace quantity of PXB 118 in one sample out of 4, 4, 2, respectively of each species analysed), and monkfish and prawns (no samples above the LOQ) have not been included in Table 12 and Figure 6.

Table 12: Levels of 2-B-7,8-CDD, 2-B-7,8-CDF, PXB-105, PXB-118, PXB-126 and PXB-156 in mackerel, farmed mussels, plaice, farmed salmon, sea reared trout and whiting* (ng/kg wet weight, upperbound)

Species	2-B-7,8-CDD (mean ± SD)	2-B-7,8-CDF (mean ± SD)	PXB-105 (mean ± SD)	PXB-118 (mean ± SD)	PXB-126 (mean ± SD)	PXB-156 (mean ± SD)
Hake	ND	ND	ND	0.020	0.007	ND
Mackerel	ND	ND	0.007 ± 0.001	0.151 ± 0.070	0.052 ± 0.023	0.019 ± 0.009
Farmed mussels	0.18 ± 0.11	0.02 ± 0.002	0.005 ± 0.000	0.011 ± 0.010	0.006 ± 0.001	0.005 ± 0.000
Plaice	ND	ND	0.005 ± 0.000	0.021 ± 0.023	0.009 ± 0.005	0.005 ± 0.000
Farmed salmon	ND	ND	0.010 ± 0.003	0.227 ± 0.101	0.084 ± 0.035	0.021 ± 0.023
Sea reared trout	ND	ND	0.007 ± 0.002	0.126 ± 0.075	0.052 ± 0.034	0.016 ± 0.009
Tuna (albacore)	ND	ND	0.005 ± 0.000	0.066 ± 0.007	0.024 ± 0.002	0.013 ± 0.003
Whiting	ND	ND	0.005 ± 0.000	0.019 ± 0.016	0.008 ± 0.005	0.006 ± 0.003

SD = Standard deviation
ND = Not detected above LOQ
* As noted in the text, data for cod, haddock, lemon sole, monkfish and prawns have not been included in this table, as the majority of samples were < LOQ

Figure 6: Mean upperbound concentration of 2-B-7,8-CDD, 2-B-7,8-CDF, PXB-105, PXB-118, PXB-126 and PXB-156 in mackerel, mussels, plaice, farmed salmon, sea reared trout and whiting (ng/kg wet weight)



5. DISCUSSION

The results of this study, undertaken to investigate levels of dioxins (PCDDs), furans (PCDFs), PCBs, PBBs, TBBPA, PBDFs, DBDPE, HBB, BTBPE, brominated dioxins and furans (PBDDs and PBDFs), and mixed PXDD/Fs and PXBs in fish available on the Irish market place, show that levels were generally low. In the case of the PCDDs, PCDFs and PCBs (both DL-PCBs and the six indicator PCBs), the levels found were well below the maximum limits laid down for these persistent contaminants (POPs) in Council Regulation 1881/2006, as amended[22]. Maximum limits have not yet been established in European legislation for any of the brominated flame retardants or related POPs; the levels found were comparable to those reported in other European and international studies, which reflect the widespread use of these compounds internationally.

This was the first study undertaken by the FSAI into levels of POPs in a wide range of fish species caught or farmed in 2010 in Irish waters, including both oily fish (mackerel, farmed salmon, sea-reared trout, tuna), and non-oily marine fish (haddock, hake, lemon sole, ling, monkfish, plaice, ray, whiting) as well as shellfish (represented by farmed mussels) and crustaceans (represented by prawns). Previous studies undertaken by the FSAI in 2001 and 2004 have focused on farmed and wild salmon, although in 2004 mackerel and fresh tuna were also sampled, together with a variety of canned and smoked tuna and salmon. Wild salmon was however unavailable for the current

survey. There are comparatively few data from other European countries on PCDD, PCDF and PCB levels in the non-oily marine fish surveyed in this study[14], although the UK Food Standards Agency has carried out an extensive study into levels of a wide range of environmental contaminants in Scottish marine and freshwater fin fish and shellfish[57]. A very wide range of POPs was also surveyed in the present study, including the brominated flame retardants recommended by EFSA for inclusion in any monitoring programme of this nature, and also the mixed halogenated dioxins, furans and biphenyls, for which few data on the occurrence in fish are available.

In considering the data generated on the PCDDs, PCDFs and PCBs in this study, as already indicated, measured levels were well below the maximum limits laid down in Council Regulation 1881/2006 (Table 5 in comparison with Table 3), the mean sum of PCDD/F and DL-PCBs in farmed salmon (the species with the highest content of these contaminants) in 2005 WHO TEQ being 1.47 $\pm$ 0.55 ng/kg wet weight, compared with a legal limit of 6.5 ng/kg wet weight. Legal limits for the sum of six indicator PCBs have comparatively recently been introduced into legislation (Table 3), and as with the PCDDs, PCDFs and DL-PCBs, levels of these indicator pollutants were well below the statutory limits, with 11.1 $\pm$ 4.06 µg/kg wet weight being detected in farmed salmon (Table 5), compared with the legal limit of 75 µg/kg wet weight. Levels of PCDDs, PCDFs and PCBs in the non-oily marine species surveyed, and also in farmed mussels and crustaceans were much lower than those found in the four oily species surveyed, reflecting the fact that these lipophilic contaminants accumulate in fatty tissues, and concentrations are therefore generally higher in foods with a high fat content.

Comparison of the levels of PCDDs, PCDFs and PCBs in farmed salmon over the period 2001 – 2010 showed a marked decline, as shown by Figure 3. A direct comparison is hampered by the fact that the analytical Limits of Quantitation (LOQ) were different in the three studies undertaken during the period, with consequential higher upperbound values being reported in the earlier studies. Despite this consideration, a 2- to 3-fold decline in levels over the period can be noted. It can be attributed to more stringent controls on industrial emissions of these POPs, together with the maximum limits introduced for feed used in aquaculture, feed being an important source of contamination in farmed salmon prior to introductions of such limits. Recent data from EFSA[14] have shown that overall in the EU, farmed salmon and trout are now significantly less contaminated with dioxins, Dl-PCBs and the six NDL-indicator PCBs than wild caught salmon and trout, a finding which probably reflects the ongoing high levels of contaminants in the wild species from the Baltic Sea. It should be noted however, that the levels in found in farmed salmon in this study were still approximately twice those found in Irish wild salmon in 2004. Concentrations of PCBs, PCDD and PCDFs were lower in albacore tuna than determined in the 2010 survey, but similar for mackerel.

It should be noted that while the mussels investigated in this study were cultivated, the food sources of farmed mussels are the same as wild mussels (phytoplankton and suspended organic matter), and contaminant levels therefore reflect environmental conditions in which they are cultivated. This is different from farmed fish where fish oil/meal incorporated in feed given to farmed fish is the primary source of the POP burden.

As with the PCDDs, PCDFs and PCBs, levels of the (lipophilic) brominated flame retardants measured in this study were higher in the oily fish surveyed than in the non-oily species, e.g. Tables 8, 9, 10. The predominant BDEs reported in this study, BDEs 47, 49, 99, 100, 154 and 155, were found in significant quantities in the majority of species analysed (Table 8). The highest concentrations of total BDE (sum 26) were observed in farmed Atlantic salmon (1.81 µg/kg wet weight), followed by mackerel and sea reared trout (1.02 µg/kg wet weight in both species) and

fresh tuna (0.46 µg/kg wet weight). Of the 1.81 µg/kg wet weight total BDE (sum 26) measured in farmed Atlantic salmon, BDE 47 represented 0.79 µg/kg wet weight, BDE 100 was 0.19 µg/kg wet weight, while BDE 49 BDE 99, BDE 154 and BDE 155 were 0.18, 0.17, 0.15 and 0.10 µg/kg wet weight respectively. Similar findings have been reported in surveys of fish from other European countries, including the UK. Comparison of the data for the BDEs obtained by the FSAI in 2004 with the current data is difficult, since again the LOQs differed and additionally, 26 BDE congeners were surveyed in the present study, compared with 16 in 2006. However, there was an indication of a general decline in levels of BDEs over the period, which again is likely to reflect the regulatory controls introduced for these compounds over the last decade, including banning of pentaBDE mixtures. In a more recent study, the UK Food Standards Agency reported a high level of BDE-209 in mussels and other shellfish, being an order of magnitude higher than BDE 47[57]. In the current study, in contrast, levels of BDE-209 in mussels, expressed on a fat weight basis, were approximately 50% of the BDE 47 levels. The highest levels of BDE 209 found in the current study was in prawns, the level being two orders of magnitude higher than that of the other BDEs (11.7 µg/kg fat weight, compared with 0.11 µg/kg fat weight for BDE 47).

Mackerel, farmed salmon, sea reared trout, farmed mussels and to a lesser extent tuna, hake (only one pooled sample analysed) and whiting also contained the brominated flame retardant HBCD. The predominant isomer detected was α-HBCD, which comprised the majority of the total HBCD detected in these samples (Figure 5). Similar findings have also been reported in a number of other studies[30,35]. The detection of comparatively high levels of HBCD in farmed mussels is of interest, since mussels are not normally considered as high in fat, and levels of the BDEs in mussels were at the lower range of values measured, compared with the fish species investigated. HBCD had been measured in farmed salmon in the 2004 FSAI study, and as with the BDEs, a decline in levels was seen over the period, although again, direct comparison of results of the two studies is not completely appropriate.

PBBs were measured in fish for the first time in Ireland, and were only detected in mackerel, farmed mussels, plaice, farmed salmon, sea reared trout and tuna (Table 10). Of the congeners measured, only PBB-49, PBB-52, PBB-77, PBB-101 and PBB-153 were detected above the LOQ, and not all congeners were detected in the six species listed. PBB 52 was the most abundant congener, with PBB-49, PBB-101 and PBB-153 being detected at comparable levels. Farmed salmon contained the highest levels of the PBBs measured.

Of the other brominated flame retardants surveyed in this study, tetrabromo-bisphenol A (TBBPA), decabromodiphenylethane (DBDPE), hexabromobenzene (HBB) and bis(2,4,6 tribromophenoxy)ethane (BTBPE), TBBPA and HBB were not detected in any sample at levels above the LOQ, while BTBPE was detected at the LOQ (0.01 µg/kg) in one sample of mussels and at a level of 0.01 µg/kg in a sea reared trout sample. DBDPE was detected in two monkfish samples and a whiting sample, again at levels around the LOQ.

The most commonly detected brominated PBDD/PBDF congener, detected in one or more samples from every species investigated in this study, was 1,2,3,4,6,7,8-HeptabromoBDF (Table 11). For the majority of species, this was the only brominated congener detected. It was notable however, that farmed mussels and to a lesser extent farmed salmon and sea reared trout, contained measurable levels of the other brominated dioxin congeners. In the case of mussels, this may be due to metabolic differences and/or the filter feeding regime if the species, while in the case of salmon and sea reared trout, it may reflect their oily nature (although mackerel did not contain these other congeners). The PBDFs predominated, with mussels containing 2,3,7-TriBDD, 2,3,8-TriBDF, 2,3,7,8-TetraBDF,1,2,3,7,8-PentaBDF and 2,3,4,7,8-PentaBDF as well as

1,2,3,4,6,7,8-HeptabromoBDF.The mean derived upperbound WHO TEQ attributable to PBDDs, and PBDFs for the majority of species surveyed in the study was 0.015 pg/g wet weight, the value for mussels was 0.020 ± 0.003, for salmon 0.020 ± 0.002 and for sea reared trout 0.022 ± 0.006.

Analysis of the mixed PXDD/Fs and PXBs provided some interesting results. Few data are available on the occurrence of the mixed halogenated dioxins, furans and biphenyls in fish, although both the FSAI[7]and the UK Food Standards Agency[57,58] have published data on occurrence in a range of other foods. These compounds are reported to be at least equipotent as the PCDDs, PCDFs and DL-PCB in terms of the biological effects observed in animal and in vitro studies. Of the mixed halogenated dioxins and furans measured, only 2-B-7,8-CDD and 2-B-7,8-CDF were found in any sample above the LOQ, and essentially only in mussels. Four of the six mixed halogenated biphenyls (PXBs) measured in the study, PXB 105, PXB 118, PXB 126 and PXB 156, were found in mackerel, salmon, sea reared trout and tuna and occasionally in trace amounts in one or more samples of the other species investigated in the study, PXB 118 being the congener found at the highest level (Table 11 and Figure 6).

This study has not undertaken exposure estimates for PCDDs, PCDFs and DL-PCBs for the Irish population for the fishery products surveyed in this study, based on the occurrence data shown in the report. However a previous study undertaken by the FSAI[7] has shown that exposure of the average adult consumer to upperbound total WHO TEQ PCDD/Fs and DL-PCBs, derived from consumption of eggs, dairy products, meat, offal, vegetable oil and fish produced in Ireland, is approximately 2.8 pg/kg bw per week. This intake, when compared to the Tolerable Weekly Intake for the sum of PCDDs, PCDFs and DL-PCBs of 14 pg WHO-TEQ/kg body weight established by the SCF, is approximately 21% of the TWI, and exposure of the above average consumer (P97.5) is estimated at 11.3 pg/kg bw per week, representing approximately 80% of the tolerable weekly intake. The Marine Institute also conducted a preliminary assessment of intake of PCDD/F and DL-PCBs for the average Irish adult seafood consumer (excluding non seafood consumers) taking into account a detailed seafood consumption pattern and estimated that seafood accounted for about 17% of the Tolerable Weekly Intake[9]. Since the data provided in the current report suggest decreasing levels of these contaminants in Irish fish, in line with predominantly downward trends for environmental concentrations of PCBs as determined in marine monitoring programmes[59], it can be deduced that the intake of PCDDs, PCDFs and DL-PCBs is likely to have reduced further since these exposure estimates were made in 2010.

EFSA has undertaken hazard characterisations or risk assessments of the majority of the brominated flame retardants measured in this study. EFSA concluded that current dietary exposure in the EU to BDE-47, BDE-153 and BDE-209 was not of concern, based on MOEs of larger than 2.5, the value which EFSA concluded might indicate that there is no health concern. However the MOEs for BDE-99 for young children (1-3 years) were only 1.4 and 0.7 for average and high consumers respectively, and EFSA concluded that there is a potential health concern for this population group[28]. Levels of BDE-99 in Irish fish were generally low (Table 2), and given that fish consumption by the Irish population is also lower than the European average it is unlikely that intake of any of the BDEs from fish is of health concern. Similar conclusions can be reached for HBCD, PBBs and TBBPA, given that EFSA has concluded that current dietary exposure in the EU to these compounds is not of concern. There are insufficient data on both exposure and toxicological effects of PBDFs, DBDPE, HBB, BTBPE and the mixed PXDD/Fs and PXBs to be able to carry out a risk assessment.

6. CONCLUSIONS

This study has demonstrated that levels of dioxins, furans and PCBs (both DL-PCBs and the indicator PCBs 28, 52, 101, 138, 153, and 180) in Irish fish, farmed mussels and prawns are well below the relevant legislative limits for these contaminants. The results of the study are in line with those from previous FSAI studies on dioxin levels in fish and also studies on meat, milk, and eggs, and confirm that dioxin levels in these foods are relatively low compared with data for similar products from more industrialised countries in the European Union.

Overall, based on the results of this study in fish and previous studies undertaken by the FSAI on other foods potentially containing these POPs including meat, dairy products and eggs, and reflecting the fact that environmental levels of POPs have decreased substantially over the last decade due to the introduction of stringent controls, the FSAI concludes that the exposure of Irish consumers to dioxins, furans and PCBs is likely to be well below the Provisional Monthly Tolerable Intake of 70pg/kg established by the WHO.

This study has also investigated a wide range of brominated flame retardants used in industrial and consumer products in recent years, and has demonstrated that compounds such as the BDEs, HBCD and PBBs can be detected in Irish fish, particularly oily fish. The levels found were comparable to those reported in other European and international studies, which reflect the widespread use of these compounds. The study has also demonstrated the presence of trace levels of brominated dioxins and furans (PBDDs and PBDFs) and mixed halogenated dioxins, furans and biphenyls in fish. The FSAI concludes that it is unlikely that intake of any of these brominated POPs is of health concern for the Irish population.

The levels of contaminants were somewhat higher in the oily fish examined in this survey, namely farmed salmon, sea reared trout, mackerel and tuna, compared with the extensive range of non-oily fish such as cod, hake, lemon sole and whiting also investigated. However, there are particular health benefits associated with consuming oily fish due to their high contents of polyunsaturated fatty acids (PUFAs)[1]. Consumption of oily fish benefits the cardiovascular system, and also brain and eye development in the fetus and infant, and the FSAI recommends that consumers should eat at least two portions of fish per week, including at least one serving of oily fish, e.g. salmon, trout, herring or mackerel.

The FSAI is pleased to report these results and to note that Irish produce readily complies with legislation in this area. These findings support the interpretation that exposure of consumers of Irish food to dioxins is likely to be lower than the European average, a conclusion which should be reassuring to Irish consumers.

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